JOURNAL OF

THE INSTITUTE OF PETROLEUM

FOUNDED 1913+INCORPORATED 1914

Vol. 37 JULY 1951 No. 331

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Published by the Institute of Petroleum

Address: Manson House, 26 Portland Place, London, W.1

Telephone No.: LANgham 2250

Telegraphic Address: Instpetech, Westdo, London

Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk

Price 10s. 0d. Annual Subscription £4 14s. 6d. (Post Free)

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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on April 11, 1951, the chair being taken by the president, Mr C. A. P. Southwell, M.C. At the opening of the meeting Professor J. S. S. Brame, C.B.E., was installed as an Honorary Fellow.

INSTALLATION OF PROFESSOR J. S. S. BRAME, C.B.E., AS HONORARY FELLOW

THE PRESIDENT: We are honoured to have with us at this meeting Professor Brame and also Mrs Brame. (*Acclamation.*) Professor Brame joined our Institute in 1916, and he was proposed for membership by our Founder-President, Sir Boverton Redwood, and seconded by Mr Arthur W. Eastlake, who was then the Honorary Secretary. To those two gentlemen we owe all that early spade work in the formation and foundation of our Institute, so that in Professor Brame we have a link with the very beginning of the Institute.

Professor Brame was our fifth President. He took office in 1921, following Sir Frederick W. Black, and throughout the whole time that he has been active with the Institute he has been one of our ablest speakers and one of our ablest councillors. He was the second chairman of the Standardization Committee, and it is most appropriate that to-night we have a meeting on standardization and that Professor Brame should come here on this occasion to be with us again and be installed as an Honorary Fellow.

It is rather interesting to look back into the records of the Institute to the evening of the Fifty-fifth General Meeting, when Professor Brame said: "*There are two large and important questions on standardization—specification and testing methods. These can only be satisfactorily dealt with in co-operation with other bodies in the United States and elsewhere,*" and he hoped that it would be possible during his term of office to arrange such co-operation and begin that important work. To-day, some thirty years later, whilst a vast amount of work has been done on standardization by the Institute, we are still exploring what steps we can take in order to ensure that we have better and better co-operation, particularly with our American friends, who have gone such a long way on standardization in recent years.

Professor Brame made, of course, many excellent speeches both as President and as a Member of Council, and in one of those speeches he quoted a saying of King David that "oil giveth a man a cheerful countenance," but I do not think at that time he thought that thirty years later we would regard him as the most perfect example of that, in that he has always had a most cheerful countenance whenever he has dealt with anything concerned with the Institute. (*Hear, hear!*)

Now the growth of the petroleum industry in the past thirty years has been prodigious. If we think back to the time when Professor Brame was

President, world production was less than one hundred million tons—to-day it is five times that amount. Our membership is now five times what it was when Professor Brame was President, but we are making every endeavour at the present time to see that our membership is considerably increased. At that time no oil was being produced in Great Britain, although admittedly about three years later oil was found here. But there was no real refining industry, and now we are entering upon a phase of a very large refining industry.

It had been planned to-night that Dr A. E. Dunstan, one of Professor Brame's oldest friends and colleagues on the Council of the Institute, would be here in order to welcome him and to say a few words. On medical advice Dr Dunstan has not been able to come, but he wrote me a letter to say how sorry he was and which reads : " So sorry I shall miss the meeting on Wednesday but my doctor is adamant against my turning out during a phase of high blood pressure—the old man's disease. Luckily it is not really serious but one must avoid excitement, and the sight of Brame and other old friends might put the mercury up a few millimetres. As soon as the weather improves I shall shed my chrysalis and emerge at 26 Portland Place." Knowing Dr Dunstan as I do, and as Professor Brame knows him, it is quite obvious that despite his illness at the present time he has not lost one atom of his spirit.

We are very honoured to make Professor Brame an Honorary Fellow of the Institute of Petroleum as a very small recognition of the great work that he did us for in the past, and I am sure we are all very glad to see him here looking, in his customary way, fit and well and, I might add, benevolent. I will now, on behalf of all our members, ask him if he will be good enough to sign the Book of Honour as an Honorary Fellow.

Professor Brame signed the Book of Honour amid prolonged acclamation.

PROFESSOR J. S. S. BRAME, C.B.E. : I am not going to detain you with a speech this evening as there are many important matters to be discussed in connexion with standardization in which you are particularly interested. In years gone by, as the President has already told you, I was also interested in that subject, and we were able to establish contact with our United States friends, particularly with Dr R. P. Anderson of the ASTM.

I should like now to say a word or two about the help which was given to the Institute and to the members personally by Dr Dunstan. He was always a busy man, but full of energy, and no one could have done more for the Institute than him. He would certainly have been here to-night had it been possible. He was assisted, particularly with the *Journal*, though with much of the technical work also, by George Sell, who is still in the service of the Institute.

It is interesting to look back at the homes which our Institute has had the past. In the early days the Council Meetings were generally held in the offices in Gracechurch Street occupied by Mr Arthur W. Eastlake, the first Honorary Secretary, and it was a very frequent thing for a meeting to consist of four or five members—Sir Boverton Redwood, Arthur W. Eastlake, Dr A. E. Dunstan, Dr W. R. Ormandy, and myself.

So we began in that very small way. The next step was to move into John Street, Adelphi, right opposite the house of the Royal Society of Arts,

where our general meetings were then held. From there we went to Bedford Street, then we moved to the new Adelphi building, and from there into this building.

One of the things which I know is foremost in the minds of the President and most of the members is that the Institute shall some day have its own house and keep its own house in order. I hope to live to see that.

I would like to express my thanks to the Council and to all the members of the Institute for the honour which they have conferred upon me in making me an Honorary Fellow of the Institute.

Professor Brame withdrew from the meeting amid acclamation.

A SYMPOSIUM ON STANDARDIZATION

The chair was then taken by Mr E. A. Evans, past-president and chairman of the Standardization Committee.

THE CHAIRMAN: From time to time the Standardization Committee takes an opportunity to bring to the notice of the members of the Institute some phase of its activities. This evening we are bringing before you the work of four of the sub-committees. There is no direct connexion between the papers which are being presented this evening, and we are not asking the authors to read them. We have asked Mr W. H. Thomas, one of our indefatigable workers, to produce a report on the four papers.

MR W. H. THOMAS then introduced the four papers which follow.

THE WORK AND PROGRAMME OF SUB-COMMITTEE No. 2. CRUDE OIL

By H. JAGGER (Associate Member)

INTRODUCTION

THE Crude Oil Sub-Committee was re-constituted in December 1946 after a lapse of nearly four years, due no doubt, to the considerable reduction in domestic refining activities which resulted from wartime conditions.

The position to-day is much as it was in 1946, in that the Sub-Committee is directly responsible for only five tests. It is a small committee and has no permanent working Panel. This is no measure of the Sub-Committee's activities, but is, it may be suggested, an indication of the place which crude oil has occupied in Britain in relation to petroleum products until the recent rapid increases in refining capacity.

There are, however, many additional tests applied to crude oil. These are the direct responsibility of other sub-committees, but the Crude Oil Sub-Committee is indirectly responsible and ensures that these tests, and

suggested changes to them, are such that they are suitable for the testing of crude oil. In this connexion it undertakes co-operative testing where a need is indicated and, if necessary, makes recommendations to those sub-committees responsible for tests not under its own direct control.

The main justification for a crude oil sub-committee would appear to be the necessity for special tests for crude oil. These remarks will therefore be confined to those tests for which the Sub-Committee is directly responsible. The work which has been done and is being done to modify these tests to meet present-day requirements, including the work done by the crude oil Evaluation Panel and the future programme of the Sub-Committee, are described.

Past Work

When the Crude Oil Sub-Committee was re-formed in 1946, doubts existed as to the demand for tests of the type which then appeared in " Standard Methods " for the distillation of crude petroleum and crude petroleum residues. On the other hand, with the tremendous increase in domestic refineries which was then being planned, it was obvious that some standard procedure for the evaluation of crude oil was desirable. The Sub-Committee approached the major oil companies, who co-operated wholeheartedly and put details of their respective methods of evaluation at its disposal.

It was immediately evident that the evaluation of crude oil could not be carried out on a small scale and in apparatus which could be obtained for small capital cost. It was also confirmed that none of the major oil companies were using the method set out as IP 25/44 (P). A Panel was therefore formed with the object of considering methods for the evaluation of crudes and to formulate a recommended procedure.

The result of the work done by this Panel has been published and comments invited. Whether at some future date a standard method for crude oil evaluation can be produced, will depend on the comments received. The Sub-Committee is convinced that the method previously published was not used and in fact, could not be used satisfactorily, to meet the refiner's need for a comprehensive evaluation of crude oil.

A notice of withdrawal of IP 25/44 (P) was published in the 1950 " Standard Methods," and in the absence of any request to the contrary the method has been omitted from the 1951 edition. The Sub-Committee can claim some credit for being ahead of the ASTM in respect of crude evaluation. It has reason to believe that consideration has been given to this question by its counterpart in the U.S., but is unaware of any publication on the subject from that source.

While its Crude Evaluation Panel was busy with crude oil evaluation, the Sub-Committee spent considerable time on the determination of salt content of crude oil. Two modifications to this method have been made in recent years.

Both the method of extraction and of testing for chloride have been modified and provision made for removal of sulphide if this is present.

The Panel's work on this test has not been influenced by any considerations for standardization with our friends in the U.S., as there is no corresponding ASTM method. Some American refiners are working on

similar lines to those adopted in the 1951 edition of "Standard Methods," as has been indicated by published articles on salt determination in American journals.

One other test, that for water and sediment by centrifuge, has also been subject to some modification. The increase in production, and consequently in refining, in this country particularly, of waxy crude oils, has necessitated changes to the procedure if wax is to be excluded from the result of this test. Co-operative work by members of the Sub-Committee confirmed that wax could be excluded by relatively slight changes in the pre-treatment temperatures.

It is believed that the IP is in line with the ASTM in its modifications, and that body has been advised of the IP intentions in the hopes of achieving agreement in the modification of test procedure if it is intended to exclude wax from the test result.

Present Work

It has already been indicated that the question of crude-oil evaluation has been dealt with in some detail, and that criticism, preferably constructive, of the published recommended procedure is awaited with interest. The methods adopted are such as will give a detailed indication of the quantity and quality of products which can, according to the refiner's resources, be obtained from a given crude oil. It does not indicate to what extent the crude may be expected to give rise to corrosion troubles either in storage or when processed. The committee is therefore concerned with the development of methods for the determination of hydrogen sulphide and of mercaptans present in crude oil, and also of methods which will indicate the probability of these compounds and of hydrochloric and naphthenic acids being released when the crude is distilled under normal plant conditions. It is in connexion with these requirements that considerable co-operative work has been done, and the results are, it is believed, such as will enable the making of recommendations on the method of test for hydrogen sulphide, if it is to be suitable for use in the presence of mercaptans.

The methods for potential corrosive materials in crude oil, *i.e.*, those that will be formed under distillation conditions, are in a much earlier stage of development, and may very well be the subject of consideration and co-operative work for some months to come.

In developing tests for hydrogen sulphide and other corrosive materials, either existent or potentially present in crude, the Sub-Committee's prime concern is the means of separating these compounds from the crude. Work is in close collaboration with the Sulphur Panel and other expert bodies of the Institute whose special knowledge will be utilized with pleasure once a separation is obtained.

Future Work

At the beginning of this report, it was stated that the committee in 1946 had doubts as to the value of the methods for distillation of crude petroleum and for distillation of petroleum residues. Since that date, as has been

indicated earlier, the method for distillation of crude petroleum has been deleted and the paper on crude-oil evaluation published.

It is felt that there may still be a demand for a small-scale, vacuum distillation of crude residues, but it is thought that the method suggested in IP 78/44 requires considerable modification and amplification if it is to remain in "Standard Methods." Comments on the usefulness or otherwise of this method would be welcomed by the Sub-Committee.

The method published as IP 24/44 for the Preliminary Distillation of Crude Petroleum differs considerably from the methods of distillation for petroleum products and also from the corresponding ASTM method. There are indications that the procedure given in "Standard Methods" is used only by a limited number of people. The Sub-Committee would welcome further information on the extent to which this test is followed in the industry with a view to adapting it to use either a standard apparatus for product distillation or the ASTM apparatus.

Frequent reference has been made in this report to ASTM methods and the desire to obtain close agreement with these. British and American interests are so closely concerned in the production, marketing, and refining of crude oil, that the committee is convinced that the welfare of the industry can best be served by a co-operation between the IP and ASTM, and if possible, by a complete unification of test methods. Future policy will be to obtain as much standardization as is possible consistent with meeting all the requirement of British producers, marketers, and refiners. Direct contact with chairmen of technical committees of the ASTM will be maintained to ensure full co-operation.

THE WORK AND PROGRAMME OF SUB-COMMITTEE No. 4. GAS, DIESEL, AND FUEL OIL

By H. GARDNER (Fellow)

THE work of the Asphaltenes Panel had its inception in an investigation of the difficulties encountered in the examination of certain waxy products. In the then existing method, wax precipitated with the asphaltenes was removed by washing, on the filter-paper, with hot alcohol. In the case of certain high-melting-point waxes such a procedure did not procure complete removal of the wax, and the current procedure of extracting, under reflux, with IP spirit was found to be satisfactory in all cases. The accuracy of the determination of very small quantities of asphaltenes was improved by specifying the evaporation of the final benzene solution in an open dish instead of, as hitherto, by distillation from a conical flask. In this way the removal of the last traces of solvent is greatly facilitated.

The Panel has always confined itself to asphaltenes in oils, but is conscious of the undesirability of the present position in which a separate method exists for the examination of bitumen. It is hoped that, finally, a method applicable to all asphaltic materials will be evolved.

In its more recent work, which is still incomplete, the Panel's activities have been under two headings: (*a*) the method of distilling a crude oil to remove light fractions which would interfere with the precipitation of asphaltenes and (*b*) a search for a pure hydrocarbon, readily available at a reasonable price, which would replace IP spirit, the specification of which is arbitrary and difficult to define with adequate precision.

The work under (*a*) was quickly brought to a satisfactory conclusion by recommending the distillation of a crude oil to an *oil temperature* of 260° C instead of an *overhead temperature* of 200° C. By this change in procedure the danger of overheating the residue and thereby affecting the asphaltene content of the residue is reduced to a minimum. Co-operative work in several laboratories on eleven different crudes indicated that the changed procedure does not affect the volume of the distillation residue.

In the matter of the precipitant used for the separation of asphaltenes there is a firmly fixed impression that IP spirit prepared from different crudes, although complying with the specification, may be of sufficiently different hydrocarbon composition as to yield different results one from another. This impression is not easy to document, but the advantages of using a pure hydrocarbon for this purpose are obvious.

It was a necessary proviso that the order of the result obtained should not be altered significantly by using an alternative to IP spirit.

Preliminary work with *iso*-octane and *n*-heptane indicated that the former hydrocarbon was unsuitable for this reason. The deviation of the results from those with IP spirit was over the range +150 per cent to −33 per cent. With *n*-heptane the deviation was over the range +19 per cent to −33 per cent the majority of the results being within the range +13 per cent to −7 per cent. It was therefore decided that if the accuracy of the determination was at least as good with *n*-heptane as with I.P. spirit, *n*-heptane would probably satisfy requirements. The results of an extensive programme of co-operative work were examined statistically with results which indicated that reproducibility was a long way from the standard indicated by the limits given in IP 6/49. However, the present limits were based somewhat arbitrarily on general experience, and the Panel is at present engaged on actually determining the reproducibility of IP 6/49 with IP spirit. It is considered likely that the published limits may be found to be somewhat optimistic, in which case still more work will be necessary in an attempt to improve accuracy.

Fuel Oil Stability Panel

Interest in the stability and more particularly the compatibility of fuel was brought to a head during the last war, when it became necessary to bunker naval vessels on both sides of the Atlantic as well as in the Near and Far East. It was in these circumstances that the NBTL Test (National Boiler and Turbine Laboratory) came into the picture. The Panel's early activities are dealt with in its report published in the *Journal*,* which gives an account of investigations into several methods of assessing stability.

Progress since then has been slow. Recommendations for definition of the various recognized types of instability have been made, but little head-

* *J. Inst. Petrol.*, 1945, **31**, 347–52.

way has been made in methods of either assessing inherent stability or forecasting probable stability under conditions known to provoke instability. The NBTL Heater Test is under consideration, and it is hoped that an agreed draft of this method will be ready as a tentative standard before long.

This is not to be construed as indicating that the Panel is entirely satisfied with that test, but while it is an official acceptance test of the U.S. Navy and British Admiralty it is worthy of the attention of the Institute of Petroleum. The biggest disadvantage of the test is probably the arbitrary and qualitative nature of the assessment of the final result. Attempts have been made to put it on a quantitative basis, but these have not been entirely satisfactory.

The frank position is that there is no generally accepted stability test. Many tests have been suggested, and all fuel laboratories have tests which suffice as expedients for local control. All have this in common that they attempt to simulate the cause of instability, to accelerate the process, and finally to measure the effect in terms of the amount of solid dispersed material formed. Filters and centrifuges are available for the latter purpose, but difficulties are introduced by the need to remove oil from the residue and the absence of a sharp differentiation between solid and non-solid components in the oil. In addition, both processes are limited by the viscosity of the oil. In this connexion the Panel severely criticizes the usual B.S. & W. Test, in which the limited affect of high viscosity is overcome by diluting with benzole. Such dilution involves the risk of reducing the amount of solid matter and may increase it by precipitation. Where the viscosity of the oil is low enough at the temperature of treatment, centrifuging is considered to be a reliable means for the quantitative removal of solids. An alternative process is the Hot Filtration Test, in which the undiluted oil is filtered, either through paper or a filter mat, under a pressure differential, and the Panel has this test under active consideration.

It must be emphasized that neither of these procedures are stability tests in the strict sense. Both may assess the condition of an oil as received or after some form of pretreatment, but the complex problem of what is likely to happen to an oil when it is stored, or heated or blended remains little understood, and the subject of piecemeal and arbitrary attack whenever it occurs.

Calorific Value

Standard Method 12/51 is noteworthy in giving, for the first time in "Standard Methods," the complete specification for the bomb which is also used in IP 61/49—sulphur content. The method defines the terms "gross califoric value," "net calorific value," and very necessarily, the unit in which the result is reported. The method prescribes benzoic acid as the thermo-chemical standard, and includes the specification for that standard.

Recommendations are made in accordance with current ideas on "safety at the design stage" and for the control of maximum potential pressure within the bomb during its operation.

The method does not constitute any advance in the technique of deter-

mining calorific values, but the very complete specification now published provides for a much-needed tidying-up of procedure which should make for greater conformity of practice in different laboratories.

It is a sobering thought, however, that, simple though a calorific-value determination is in principle, it is one which occasions more heartaches in the form of unaccountable freak results than, probably, any other commonly made determination. There is a well-founded impression that the value can be as accurately calculated as determined and with a considerable economy of effort. If the new standard method does anything to dispel this impression the Panel will be well rewarded. If it does not there is a clear case for examining the whole question of the determination, since not all materials lend themselves to assessment by calculation from more simple characteristics.

Fuel Oil Flow Panel

Existing methods for the determination of viscosity are unreliable when used at temperatures at which, usually as the result of the presence of crystallized wax, the oil possesses a structure. It is well known that the repeatability of the Redwood viscosity determination is bad at 100° F or lower temperatures on certain types of oil and, when first formed, the Panel was charged with the responsibility of developing a method of pretreatment which should bring such an oil into such a condition as would render the reliable determination of its viscosity possible. Various combinations of heating and mechanical agitation were tried without success, nor was a U-tube viscometer found to be any more reliable than the Redwood instrument. The Panel, accordingly, recommended that 122° F, at which temperature wax could be assumed to be in solution, should be the minimum at which the viscosity of a fuel oil should be determined. This was a most unsatisfactory position. Data are frequently required concerning pumpability. Fuel in a system may not be pumpable at ambient temperatures, and it is necessary to know to what minimum temperature the oil must be heated in order that pumping may be commenced. It would be insufficient to determine the viscosity at elevated temperatures at which the property was normal and extrapolate to an accepted figure representing the limit of mobility.

The Panel was therefore reconstituted to approach the problem *de novo*. That approach has been somewhat revolutionary. The two mobility tests at present in use are pour point and viscosity. It has hitherto been the aim of the pretreatment stages of those tests to bring the oil to a condition of maximum or minimum mobility at the measured temperature. In practice the condition of the oil is likely to attain to an intermediate condition. The Panel decided that the pour test was sound for its purpose, but that neither the maximum nor minimum figures were likely to be of practical use. Recommendations based on the minimum figure would tend to be too lenient, while those based on the maximum would be too restrictive. Work was therefore put in hand to develop a pretreatment process which would bring an oil to the physical condition it would acquire in quiescent storage at ambient temperature and immediately ran into the difficulty of determining what the condition is. However, progress has been made. Already it has been made clear that the present standard

method for determining the maximum pour point may not be correct, since it appears that the oil's condition of ultimate mobility is a function of the pretreatment temperature and passes through a minimum at a temperature between 100° and 200° F. Moreover, this optimum temperature varies with different oils.

Concurrently, work with coni-cylindrical rotating viscometers has indicated that when a waxy fuel oil has been fully broken-down by continuous shearing at a constant temperature under a particular shearing stress, the flow is approximately Newtonian over a range of shearing stresses not too far removed from that applied during the break-down. The value of the limiting viscosity reached under such conditions should determine the ultimate rate of pumping of the fuel oil at the same temperature and under a similar shearing stress in practice. By making tests at different temperatures under a shearing stress representative of those occurring in practice it should be possible to obtain a reliable indication of the minimum temperature at which a given fuel oil can be pumped at an economical rate through pipelines under average practical conditions.

It is hoped that a simple test for the pumpability of a fuel oil can be evolved on the above lines. Further consideration has to be given, however, to the question of the flow of the oil within the storage tank to the suction pipe, where the possibility of cavitation arises.

This concludes the survey of the methods which are the direct responsibility of the Sub-Committee No. 4 as the sponsoring body, but at least two other methods of interest to the Sub-Committee call for comment.

Cloud Point

Standard Method 15/42 is considered to be inadequate in two respects.

(*a*) Instructions for drying samples are inadequate, it being insufficient merely to filter an oil through paper.

(*b*) The method does not cater for dark oils, procedures for dealing with which are in current use in the industry.

Sulphur Content

Standard Method 63/51 calls for comment on one or two points.

(*a*) The temperature of the reaction zone of the tube is inadequately specified. This temperature is one of the most important factors in the test, and its specification in such qualitative terms as " bright-redness " is regrettable. It is suggested that the temperature should be specified as 950°–1000° C. Experience shows that lower temperature leads to unreliable results. This raises the question of the method of heating. Gas is seldom adequate. Only electrical heating can be relied upon to provide adequate temperature, and if it is not practical to specify electrical heating the method should at least stress the importance of maintaining a minimum temperature of 950° C and the advantage, in this respect, of electical heating.

(*b*) The air-purification train is not necessarily adequate. Combined sulphur and chlorine unaffected by 50 per cent sulphuric acid and 30 per cent caustic soda will not be removed. The method should specify the use of a second tube in parallel, as a blank, or in series, in front of the air-purification train.

THE WORK AND PROGRAMME OF SUB-COMMITTEE No. 9. DERIVED CHEMICALS

By P. J. GARNER (Fellow)

SCOPE

THE terms of reference of this Sub-Committee are defined as follows: the examination and development of tests on chemicals derived from petroleum such as are already marketed. On this basis the following existing IP methods come within its scope :—

IP 95 Alkalinity.
93 Drying time of aromatic petroleum extracts.
94 Inorganic salts in detergents of the alkyl sulphate type.
86 Mean molecular weight.
87 Naphthenic acids in soda-neutralized oils.
88 Peroxide value of ethers.
89 Residual odour of lacquer solvents.
90 Surfaces and interfacial tension measurements.
99 Unsaponifiable matter in drying oils.
92 Wetting power of wetting agents derived from petroleum.

ORGANIZATION

In order to facilitate the operation of the Sub-Committee, the work is divided between two panels, the Chemical Tests Panel (B) and the Technological Tests Panel (C). A Physical Tests Panel (A) was formerly in existence, but was disbanded in 1948, its work being taken over in the main by Panel C.

CHEMICAL TESTS PANEL (B)

For some years the main work of this Panel has been the development of a comprehensive method of analysis for sodium naphthasulphonates (petroleum sulphonates). As marketed, these materials consist of a complex mixture of organic sulphonates, carboxylates, oil, water, and inorganic salts. The analysis was found to be unexpectedly difficult, partly due to the colloidal nature of the system, partly to the difficulty of representative sampling, and partly to the fact that the high-molecular-weight sulphonates are very difficult to separate from the mineral oil.

Since 1944 six methods have been examined by the Panel, and co-operative tests arranged on four of them. It is gratifying to report that one method has now been selected and drafted by the Panel and will be submitted to the Sub-Committee in the near future. In addition to this, another method of analysis which at present is not considered to have the accuracy of the selected method, but has the advantage of greater rapidity, is the subject of further development work by the Panel.

The Panel has been in contact with Sub-Committee No. 6 Miscellaneous Tests Panel with regard to the development of a comprehensive method

for the determination of saponifiables and unsaponifiables in oils. As a result of the contact, it is expected that an anomaly in the existing method, IP 52, will be eliminated.

The Panel proposes to look into the possibility of providing methods for the analysis of water-soluble detergents of petroleum origin, which materials have assumed great commercial importance in recent years.

Technological Tests Panel (C)

This Panel has been mainly concerned with the development of a method of determining the rate of evaporation of solvents. Contact with the Oil and Colour Chemists' Association (OCCA) on this problem is being maintained.

THE WORK AND PROGRAMME OF SUB-COMMITTEE No. 12. GREASES

By E. G. Ellis (Fellow)

Introduction

The Sub-Committee was formed in 1945 and replaced the Grease Panel of Sub-Committee No. 6. The original twenty-four members were chosen so as to represent equally producers, commercial users, and the Ministries. This representation was extended also to the membership of the three Panels, and arrangements were made whereby other interested groups would be kept advised of progress and where necessary joint action taken at either Panel or Working Group level. It was agreed to make contacts with corresponding standardizing bodies such as the BSI, ASTM, etc. The amount of work required from the Panels has steadily increased, and it is gratifying to record that the membership has kept pace with it.

Work of the Panels

The General Test Panel is almost the direct heir of the older body of the Grease Panel of Sub-Committee No. 6. It has studied, and will no doubt continue to do so, the largest number of methods and has made extremely good progress in the five years of its very active life. The work of the Mechanical and Rheological Tests panels has been qualitatively rather different. The need for test methods which give information of actual performance of greases has become more and more apparent over the last few years. Originally stimulated by the wartime demands of the Services, such requirements have extended and are to-day becoming permanent features of specifications. The measurement of flow properties of greases is a good example, as its connexion with lubricant dispensing is clearly seen. Tests are also required which will indicate the behaviour of greases in bearings at high and low temperature or for extended periods at various

speeds and loads. The development of such tests is usually a long-term project frequently requiring expensive and elaborate equipment which makes co-operative work difficult to arrange. Other methods, particularly those relating to flow, require investigation of quite a fundamental nature at times approaching true research. These and other reasons have precluded any spectacular progress being made, but the detailed reports of the work of the two panels will show the scope of the problems with which they are concerned. Lubricating greases are complex bodies and their physical behaviour difficult to define. Up to now the existing tests have been mainly empirical and demonstrably insufficient for a reliable forecast of their behaviour. It seems very necessary that thorough investigation should be undertaken before the publication of fresh tests. It is far too easy to adopt what might be called " stop-gap " methods which tend—as has so frequently happened in the past—to become standards almost before it is realized.

General Tests of Greases Panel

Matters with which the Panel has dealt are given in chronological order :—

(i) *Corrosion Test for Lubricating Greases*

This test introduced as IP 112/47 (T) was modified to IP 112/48 (T). Copper is prescribed, though other metals may be used, at temperatures not higher than 20° C below the melting point of the grease. In the modification it was recommended that with copper discolorations should be further defined as " black," " grey," or " not black or grey," and that colours other than these should not be individually recorded, as they are not significant unless they are of the first-order sequence.

(ii) *Free Alkali and Free Acid in Greases (now IP 37/47)*

A slight modification was made to this test IP 37/44 to allow of the use of 0·2*N* or 0·1*N* alcoholic potassium hydroxide if this is an advantage.

(iii) *Oil Separation on Storage of Grease*

This test, designed to determine the tendency of a lubricating grease to separate oil during storage in cans or drums, was introduced as IP 121/48. In it, a column of grease resting on a metal-gauze cone is subjected to the pressure of a 100-g weight and the amount of oil separated under standard conditions is weighed. Modifications are being made in the next edition of " Standard Methods " in regard to calculation, reporting, and precision. This test will be the subject of further study, as there has been an indication that special provision is necessary for very soft greases.

(iv) *Foreign Particles in Greases*

A method has been put forward for " Dirt Count." This is designated IP 134/51. It consists of microscopic examination of a definite volume of grease in a layer about 0·15 mm thick, the particles being graded according to size and number.

(v) *Melting Point of Petrolatum*

It was decided to recommend to Petroleum Waxes Sub-Committee No. 8 the inclusion of Method D.127–49 of ASTM Standards, in view of the lack of a specific IP method for melting point of petrolatum and microcrystalline wax.

(vi) *Drop Point of Greases*

The panel has felt for a long time that the ASTM Method D.566–42 should be included in " Standard Methods " as an alternative, as it gives rather better precision than IP 31. It is designated IP 132/51.

(vii) *Oxidation Stability of Lubricating Greases by the Oxygen-bomb Method*

The panel has carried out a good deal of work on this test, and has recently completed the experimental part of a large correlation scheme. It is hoped, when these results have been reviewed statistically, to produce recommendations for a method.

Further activities will include work on evaporation loss, analysis of greases, sampling of greases, water absorption, and resistance. Valuable help has been received from the Statistical Methods Sub-Committee, especially in regard to items (iii)–(vii) inclusive.

Mechanical Tests Panel

Mechanical tests in use or being developed at present can be divided into two main types :—

A. Tests which measure in a simple manner some relatively complex property of a grease of importance in its performance, such as behaviour under continuous shear. An example is the Shell " Rolling Stability " test.

B. Tests which simulate or even duplicate actual service conditions, *e.g.*, the high-temperature, high-speed endurance tests described in various aviation specifications.

The Panel has under examination various tests with a view to their ultimate adoption as standard methods in an improved or modified form, and the three active projects are discussed below :—

(i) *Tests for the Assessment of the Behaviour of Greases in Anti-friction Bearings at Sub-zero Temperatures*

The U.S. Service authorities introduced a bearing test during the war (AN–G–3a specification) and a modified version was later brought out in the United Kingdom (DTD. 577). Essentially these tests consist of finding the speed at which a greased bearing will rotate at a selected temperature under a given torque. The speed of rotation is of the order of a few r.p.m., since this condition obtains in service. Such tests are probably adequate to determine the order of the minimum temperature at which a grease will function satisfactorily.

The work carried out by the Panel has been concerned with attempts to specify the test bearing sufficiently to obtain an acceptable level of pre-

cision. Co-operative work has shown that the DTD. 577 test has poor reproducibility and that this is due to inadequate specification of the test bearing and not to differences between laboratories. Work is in progress to find out if improved precision can be obtained by specifying limits for such bearing characteristics as radial slackness, eccentricity, etc. Conclusions reached from this work will be relevant even if a modified form of apparatus be ultimately adopted.

(ii) *Mechanical Stability Tests*

It is generally considered that a certain minimum level of stability is required for a grease to be satisfactory in service. Co-operative work is in progress to assess the merits of two test methods developed to measure this property. These tests are the Shell "Rolling Stability" test and the Mechanical Worker test.

Work is being carried out with greases of known performance in anti-friction bearing rigs to determine the relationship, if any.

(iii) *The Development of a Bearing-rig Test for the Evaluation of Anti-friction Bearing Greases*

This subject is the most important and the most complex one under consideration. So far the activities of the Panel have mainly been restricted to discussion of requirements and design of a rig.

Bearing manufacturers in the United Kingdom have for many years employed bearing-rig tests for the evaluation of greases, the design of the particular rig being based on individual experience. These rigs, however, differ quite considerably.

The Panel is attempting to develop a simple general-purpose rig which would also serve as a screening test for the bearing makers' tests. The long-term aspect is to develop a single design which will enable the performance of anti-friction bearing greases to be evaluated under various conditions. Ultimately such a rig should supersede the various rigs now in use.

The high-speed, high-temperature rig described in certain aviation specifications (*e.g.*, AN–G–15a) is being considered as a basis for the general-purpose rig since it is or will be in fairly widespread use. It meets the essential requirements, since it provides a range of operating temperatures and will provide a range of speeds.

It does not appear likely that this apparatus in its present form will meet all requirements due to limitations of loading and bearing size. However, it is a convenient design for initial work, as it will permit of co-operative tests at an early date.

Rheological Tests Panel

At the first meeting it was agreed that the work of the Panel could be stated, in general terms, to cover methods of measuring the flow properties of greases over a wide range of rates of shear, including low rates applying to behaviour in the container, medium rates occurring during pumping, and

high rates in bearings. It was decided to limit immediate considerations to :—

A. The possibility of placing the existing cone-penetration test on a more fundamental basis and modifying the method to allow a wider range of consistencies to be measured and smaller samples to be tested.

B. Devising a simple viscosity test which would give an indication of pumpability.

Progress along these lines is summarized below.

(i) *Modification of the Penetration Method, Cone-resistance Test*

In the modified method considered by the Panel, the double cone of the existing test is substituted by a simple 90° cone which is lowered slowly into the sample until it becomes supported by the resistance of the grease, instead of being allowed to fall freely. The lowering device can be a simple attachment fitted to the conventional penetrometer.

According to Prandtl's theory of plastic flow, the maximum stress which can be supported over a plane circular area of a mass of plastic material is directly proportional to the yield stress of the material and independent of the size of the loaded area. Assuming this theory to apply under the above conditions, the value of the load on the cone divided by the cross-sectional area of the cone in the level of the grease surface, which has been termed the " cone resistance value," should also be proportional to the yield stress of the grease. In this case, the value obtained with a given grease under different loads and in containers of different sizes should be independent of the load and the size of the container. By suitable adjustments the method should be applicable to consistencies ranging from very soft to very hard and give values directly proportional to the yield stresses.

Investigations by the Panel confirmed that fairly constant cone-resistance values were obtained over a wide range of loads with samples tested in the standard worker pot, provided corrections were made for the buoyancy due to the grease displaced by the cone and for the rise in level of grease in the container as a result of this displacement. Agreement between results obtained with containers of different sizes, however, appear to be satisfactory only when the depth of penetration was limited, in accordance with Prandtl's theory to prevent the slip planes within the grease from reaching the wall and bottom of the container. When the penetration was limited in this way, no correction was found to be necessary for the rise in level of the grease.

A first series of tests on samples of a medium cup grease gave encouraging results. It was therefore arranged for a second series of tests to be made under carefully standardized conditions on three types of greases, viz., a Grade 0 aluminium-base grease, a Grade 3 soda-base grease, and a Grade 3 lime-base grease. The loads used ranged from 30 to 300 g, and all the tests were made in the standard worker pot.

A statistical analysis of the results indicated that tests with the 30-g load were unreliable, but that for loads from 60 to 300 g the resistance value was independent of the load used. The analysis disclosed, however, a systematic variation between observers.

Further work revealed that part of the trouble could be attributed to

variations in the friction of the cone shaft in its bearing, aggravated by scoring of the shaft due to the crude clamping mechanisms. It was agreed that members should endeavour to modify their apparatus to ensure free movement of the cone.

Following improvements in the mechanism, a third series of tests was arranged. Four types of greases were selected for these tests, a medium cup grease made from spindle oil, a medium cup grease made from cylinder stock, a semi-fluid aluminium-base grease, and a stiff lime-base grease.

Results of the tests have been reported by six members and await consideration by the Panel. From an analysis of the results it will be decided whether any further correlation work is necessary before the test can be recommended.

(ii) *Consistency Measurements on Small Samples*

Attention has been given to the use of the parallel plate plastometer for the measurement of yield stresses on samples of grease of the order of 3–5 g. In this method a small cylinder of grease is compressed between parallel plates under a given load, giving a circular disc of grease of small thickness. From the equilibrium thickness of the disc and its area, a calculation of the yield stress can be made.

It is hoped that it may be possible to obtain correlation between the yield stress measured in this way and the cone-resistance value. Preliminary experiments have shown the feasibility of the method but have indicated that certain greases may behave in an anomalous manner and the method needs further investigation.

(iii) *Measurement of Apparent Viscosity*

The Panel is in general agreement that although accurate data on the variation of the viscosity of greases over a wide range of rates of shear may be desirable in relation to certain applications, some simple test which would give a reliable indication of the viscosity over a restricted range of rates of shear (or even at one suitably chosen rate of shear) would be of considerable value.

With this object in view, preliminary tests have been made with a type of sinker viscometer in which a cylindrical bob, immersed in the grease held in a container of slightly larger diameter than the bob, is allowed to sink under load. The rate of fall of the bob under a given load is assumed to be proportional to the viscosity of the grease.

Satisfactory results have been obtained in this apparatus with semi-fluid greases, but with stiffer greases significance of the measurement is uncertain. Further investigation of this method will be made as a simple and inexpensive piece of apparatus would offer certain advantages.

At an early date, the Panel will review the position in regard to the use of the more elaborate capillary viscometers such as the SOD instrument, which are demanded for the testing of greases in relation to certain recent specifications. As only a limited number of laboratories possess such equipment, co-operative work is difficult to arrange.

Contact with the ASTM

Contact was recently made, by correspondence, with Technical Committee G of the ASTM, with the object of explaining the aims of the present Panel and commenting particularly on the micro-cone penetration method proposed by the ASTM, which, in the opinion of the Panel, is a highly empirical test, unlikely to correlate satisfactorily with the standard penetration test.

It appears from the reply received that Committee G has no intention of attempting any radical modification of ASTM method D217 to give an alternative method of more fundamental nature. The need to obtain more accurate measurements of both the yield stress and the viscosity of the grease, which forms the basis of the work of the present Panel, is not recognized by them, and their considerations will be directed only to methods of measuring the apparent viscosity of the grease as a means of providing data of a more fundamental character.

Discussion

B. H. Moerbeek: On the drop point of greases Mr Ellis says: "The panel has felt for a long time that the ASTM Method D.566–42 should be included in 'Standard Methods' as an alternative, as it gives rather better precision than IP 31. It is designated IP 132/51." Does that not leave us with the unpleasant situation of having two IP methods for drop point, which may lead to confusion? Many specifications say "Use the IP method," and one laboratory may use IP 31 and the other may use IP 132. They will get different results, and yet both be speaking about the IP drop point. Would it not be better to have one test only, in this case IP 130?

E. G. Ellis: It is the hope of the Sub-Committee that when the ASTM method has been tried it will be found that it is definitely better and it will be adopted as the sole method. In other words, the alternative is there on trial, and as we very frequently do in the Institute, we are optimistically hoping that in, say, twelve months' time sufficient information will have been gathered to enable the change to be made.

H. M. Davies: Is there any evidence that the ASTM method gives significantly different results from the IP method, because that is a rather important matter quite separate from a difference in precision of the two methods. While on this matter of precision I would like to add that I am pleased to see some references to statistical considerations in connexion with the work of Sub-Committees 4 and 12. I am not sure whether statistical Sub-Committee 15 co-operated with Sub-Committee 4 in regard to asphaltenes. I think so, and am not surprised to see it stated that, "The results of an extensive programme of co-operative work were examined statistically with results which indicated that reproducibility was a long way from the standard indicated by the limits given in IP 6/49." That certainly is in line with the experience of Sub-Committee 15 in connexion with a number of IP methods.

It is interesting also to read: "However, the present limits were based somewhat arbitrarily on general experience, and the Panel is at present

engaged on actually determining the reproducibility of IP 6/49 with IP spirit." I think we are all aware that most of these limits which are given in the standard methods are based rather arbitrarily on general experience. In fact, it has been suggested that they were arrived at by people gathered round a table saying, " Well, what shall we put down here ? "

I am particularly pleased to see that Sub-Committee 12 has received help on at least six methods, five in the general tests of grease and one in the rheological tests—the cone-resistance test. Mr Ellis, in referring to that particular test, said that the analysis discloses a systematic variation between the observers, but that was apparent only because in the next paragraph it is made clear that it was in fact not observers but the apparatus which caused that variation.

Finally, I would like to ask Mr Ellis to elucidate the final sentence of his paper, where he refers to the apparent difference in objective between his Sub-Committee and the ASTM.

E. G. Ellis : With regard to the first question, there is a tendency for the ASTM method to give a higher melting point. On the question regarding cone-resistance tests, the statistical analyses which we had from Mr Sears, from whom we have had a great deal of help, made us suspect that there was a difference, and possibly a mechanical difference. Therefore we arranged a meeting where everybody brought their own instruments and did their tests in each other's presence. It was amazing how crude the release mechanism of the average penetrometer is, and it was quite obvious that that was the answer. The next endeavour of the Panel has been to improve that mechanism by one method or another, and a great deal of success has been achieved.

With regard to the contact with the ASTM I am not completely documented, but I think the essential difference is that the Rheological Tests Panel has tried to deal with flow properties over a very wide range, and whereas the Americans are apparently satisfied with the arbitrary consistency test of the normal cone, they have concentrated their efforts on the capillary viscometer in order to obtain information which may help directly in prescription. I think that is really the difference.

J. F. T. Bloyt : One can think of the properties of grease generally as being concerned with a yield value and a viscosity. We, on the IP Panel, want to get simple but fundamentally sound ways of measuring both the yield value and the viscosity, while the ASTM are not interested in yield value, having been concerned only with getting a better measure of viscosity.

The Chairman : There are a large number of controversial points in the paper, are there not ? I, for one, would like to know more about IP spirit and the estimation of asphaltenes. Many of us have been very happy indeed with the use of IP spirit for a long time, and now we are suddenly told it is not recommended and we should use *n*-heptane or something else.

W. Pohl : On the question of the use of normal heptane I think it is a welcome move to try to select a pure chemical instead of a mixture, although I believe the position in regard to IP spirit is not perhaps as bad as some

people make out. I think we have no systematic data, but I recall at the beginning of the war, when we were forced to change our supplies from Continental to U.K. sources, we did quite a bit of investigation and even included in that investigation a spirit which met the IP specification in distillation but differed quite considerably in some other characteristics—notably in aromatic content—and there was very little difference in the results of sludge tests on transformer oils. That may not be true of asphaltenes, of course.

The Committee is well aware of work that is being done in other circles, but it may not be quite so generally known that other people are also thinking of this problem. The question of the selection of pure hydrocarbon is also being considered very extensively among international insulating-oil interests, and the C.I.G.R.E. (Conference Internationale Des Grands Reseaux Electriques) has been doing a considerable amount of work, investigating the use of *iso*-octane and heptane. They find that in transformer oils *iso*-octane does give rather higher results than IP spirit, but *n*-heptane gives very similar results. On the score of not being very different *n*-heptane would have the preference, but some people seem to want to get the maximum figure, and therefore they turn to *iso*-octane. Then I believe the ASTM have been investigating the use of pure hydrocarbons for the determination of sludge in used oils so that there is considerable thought being given to the use of pure hydrocarbons.

I was interested in another point in connexion with the safety of the calorific bomb. It happened a long time ago when a misguided member of our staff thought the temperature of the bomb was rising rather more rapidly than usual and getting too hot to hold. He hurriedly dropped it into a bucket of water, and when he opened it up he found he had put in IP spirit instead of water ! The bomb did survive, however.

Dr P. J. Garner : What is the specification for *n*-heptane ? It is all very well to specify pure solvents or pure compounds to be used in practical tests in laboratories, but if that is faithfully carried out it can be extremely expensive. I believe the indiscriminate use of *n*-heptane is frowned on in the U.K. because the cost is enormous. I think that should be taken into account before any of the panels lay down that a certain material should be used. It should first be ascertained whether it is available in sufficient quantity and at a price which the test justifies.

The Chairman : There is just one difference, and that is in these chemical matters we are using only a few cc, whereas in engine testing gallons are used so the cost is less important in one than to the other.

V. Biske : As regards the question of normal heptane, the experiments Mr Pohl referred to were carried out with the engine-test grade of this material, the purity of which (99 per cent or over) is, I think, adequate. Secondly, with reference to cost, I believe it to be correct that, at present, *n*-heptane of this grade is slightly cheaper than IP spirit. I would like to support Mr Pohl, as, apart from the considerations he has raised, IP spirit when purchased from commercial sources is sometimes outside the specification limit. A recent delivery of which I am aware had an aniline point of 65° C as against the permissible maximum of 62° C.

Turning now to the question of the sulphur bomb, Mr Thomas said there had been no accidents in the U.K., but I can vouch personally for one which occurred about twenty years ago. I remember firing a bomb, when standing uncomfortably near it, and the bomb entirely disintegrated, portions going through the roof and doors, whilst the stop-watch completely vanished. It might have been an extremely serious accident, and it has rather emphasized to me the importance of this matter.

Finally, there is one other test which might perhaps be considered, that is if it comes within the jurisdiction of any of the sub-committees whose work we are discussing to-day. This is in regard to the analysis of flue gases, with particular regard to SO_2 content. There are plenty of methods available, but they differ considerably among each other and, in view of possible increased interest in this matter on the part of alkali inspectors due to increased use of high-sulphur fuel oils, standardization may be thought desirable.

THE CHAIRMAN: Is it not laid down by the Ministry of Health, the method which should be used?

V. BISKE: I do not know of an officially prescribed method, there may be one.

There is also the question of the possible recovery, from acid wastes, of SO_2 for plant use, in which case the detection of the presence of SO_3 is important, a standard procedure might again be of advantage in this case.

THE CHAIRMAN: I would like to remind you that our association is not only with the ASTM. In the derived-chemicals paper we are reminded that there has been contact with the Oil and Colour Chemists' Association, so that we are dealing with many other organizations. Even on the design of the new bomb, there have been contacts with at least six different organizations.

H. JAGGER: Mr Gardner refers to one or two criticisms of the Sulphur Method IP 63/51, probably in anticipation of comment, but I would like to take him up on the ordinary bomb method for sulphur determination, which shows a difference between the IP and ASTM methods of treatment. Having fired the bomb and obtained the solution, the IP method recommends boiling before oxidation, the ASTM method does not, and specifically says that the solution should not be boiled at that stage. It seems to me that if the necessity to oxidize and make sure that all the sulphur is present as sulphate is accepted, then it is a bad thing to boil because SO_2 may be lost. Are any steps being taken to smooth out that difference?

H. GARDNER: I am aware of the difference, and I agree with the point, but I am not aware of anything that is being done to iron out that difference. Of course, it is more the concern of the Sulphur Panel than of Sub-Committee 4.

H. JAGGER: I would say I do not think the difference between the two methods is such as to give any appreciable difference in results in most cases, but in some recent work I did find rather erroneous results by the IP method, and on using the same bomb and the ASTM procedure the

results came back very nicely. The trouble, I must confess, was due to the bomb I was using, and the IP method was such that it showed up. Some sulphur had in fact attacked the bomb, but the ASTM method, in which there is quite a different procedure, was such as to compensate for that error, and if it is the case that one will stand a less perfect apparatus than the other, then that is the method to go for.

D. H. PEEL: In regard to nomenclature, there is a point in connexion with crude oils which I feel is rather important, and that is the rather loose use of the word "salt." A method is being developed for measuring what is in effect inorganic chloride content, and there has been a great tendency in industry to call that salt and write it down as NaCl, whereas it is not really present. When the method is established by the IP a distinction should be drawn between the use of the word "salt" and soluble chloride.

THE CHAIRMAN: This question of nomenclature is tremendously important. We have been called upon to form a glossary of terms for the assistance of the Forces, and particularly those in the North Atlantic Pact, so that whatever nation is dealing with petroleum products we are all talking the same language. I do hope that whatever assembly you are in, if you find somebody who is using a term which is not more or less standardized or recognized you will do your best to ensure that the proper term is used.

G. KINNER: Perhaps I could refer back to the work and programme of Sub-Committee 12. It will probably be agreed that the significance of the seemingly simple tests which have been dealt with by the General Tests of Greases Panel continues to be a matter for further study. For example, it has not yet been found possible to lay down limits for the precision of the determination of free acid and free alkali, although manufacturers and users employ these tests most frequently.

Regarding the corrosion test, I would like to inquire whether the results are thought to show satisfactory correlation with practical experience. My own finding is that "blackening" or "greying" of yellow metals in contact with grease is not so frequently encountered as "greening," a corrosive feature not assessed by IP 112/58 (T). The latter effect is a result of acidic corrosion, the other being usually associated with the presence of reactive sulphur compounds.

The ASTM has already published a method for assessment of oxidation stability using an oxygen bomb. For lime-base greases, the test results show no correlation with observations made on deterioration under actual long-term storage conditions. For these materials I would therefore suggest that the test temperature should be reduced to 60° C (in order to retain the solid state of the lubricant) and account be taken of the marked catalytic effect, in practice, of metal surfaces, particularly when these are covered by only a thin static film of grease.

Regarding "dirt count" of grease, I wondered whether the Panel had considered any assessment of the harmfulness of foreign matter of different types, *i.e.*, its abrasiveness as opposed to mere estimation of particle size.

A separate point concerns the increasing interest in the use of synthetic lubricants derived either wholly or partially from petroleum sources. At the moment the tendency is to apply to these materials those standard test

procedures which have been devised for natural petroleum products. Further experience may show this to be unsound practice, but, no doubt, the Derived Chemicals Sub-Committee has the matter in mind.

E. G. Ellis: Mr Kinner's first point regarding free acid and free alkali; it is really surprising how long that test has been studied. I believe it has been on the programme since the old days of the Grease Panel, and work is still apparently being continued on it, in the same way as many other old stagers like the saponification values of compounded oils. With regard to the question as to reducibility, I am afraid I cannot answer that at the moment, but I take it that it is under consideration. I would have to refer to the Chairman of the Panel for a complete reply.

Regarding copper corrosion, the definitions of the colours were, I think, originally based on some quite extensive work which was done by the Panel on various metals, and it was their opinion, I believe, that the earlier colours were of less ultimate importance than the actual attack which is mentioned. Does that answer your query?

The question of temperature is left very largely to the user, in which case one suits oneself, and a long-term test would probably be done at a lower temperature.

Referring to dirt particles, the question of abrasion has been considered by the Panel, but at the present moment it is felt that a count of the amount of material other than grease is sufficient for the present. I believe that tentative attempts were made to measure abrasion, either by using polished steel plates or glass slides, but I think one has to remember that the question of quantity is just as important, or may be more so, than quality. In other words a very tiny amount of abrasive material would probably do less harm than a larger amount of material which might be softer but which could block ducts and starve the bearing of grease.

With regard to the oxygen-bomb method, I do not think there is a large amount of correlation or knowledge between that oxidation and storage oxidation; that is, of course, because the test itself is not of very great age. The work that is being done by the Panel does include the presence of metals as catalysts, and it may be that when this method is finally put forward as a standard these might be included. At the present moment they are having some difficulty in getting good reproducibility, which seems to be tied up mainly with the surface area of the grease exposed in the bomb.

The Chairman: I have been associated with the standardization work since its inception, and I have had the opportunity of seeing the development of many of these tests. This corrosion test I should say without doubt is based entirely upon the old copper-strip test which was originally suggested, I think, somewhere about 1909. You can see this copper test throughout many of our activities, and we have inclined to regard it purely as corrosion. All sorts of colours have been suggested, throughout the rainbow, including "peacocking." We have got down simply to black or grey, which is a great advantage. Now I would not like to feel this is really corrosion in the ordinary sense: it has not that wider orbit of corrosion which Mr Kinner is referring to.

With regard to the dirt particles there has been a lot of work done in

another sphere on abrasion. It started in the automobile industry, particularly in the evaluation of filters. The filter makers were a little bit worried as to how they should evaluate their filters, and this work was thrown upon the Motor Industry Research Association during the time that I was its Chairman. We were soon involved in what passes through a filter. No filter is ideal, obviously, and a lot of very small particles were allowed to get through because of the cost of making a more efficient filter. After all, the manufacturer is going to pay as little as possible and give a restricted space on the car. Consequently you have an inefficient filter because of the dimension and the cost; therefore tiny particles are continuously circulating. The question arose, " do they do any damage ? " and the answer was " yes." It is really amazing the amount of damage which is done by particles only a few microns in diameter.

Mr Ellis referred to the size of the particle : if it is spherical it does not matter a great deal, but if it is angular it does matter, so microscopic examination has become important. In a ball bearing or a roller bearing it is usually alleged that it is the grease which causes the failure. It may be true, but it is often due to the solids that get in.

W. H. Thomas : Most of us can understand the essential features and uses of mechanical tests for greases, but it occurs to me to wonder what is the use of the bomb test as applied to these materials.

The test gives a measure of the time which elapses before the pressure of oxygen in the bomb falls by a certain amount; but what is the significance of the figure obtained ? Does it enable us to differentiate between greases of different qualities and stabilities, or is it merely an entirely empirical test invented for the purpose of writing a specification ?

Surely our efforts would be better and more usefully directed to the development of a pressure viscometer for greases. Such an instrument will definitely give results of considerable value not only to the manufacturer but also to the user, particularly to the owner driver, who must frequently of necessity attend to the greasing of his own motor car.

The Chairman : Might I answer that one ? I think the answer is simply this, that there is no recognized means by which you can judge the ageing of grease in storage. We know it goes dark and brown and it becomes rancid to a certain extent, but there is no ready means of testing it, and the bomb is one of these anchors in the deep sea of uncertainty. It is a signpost, and there is nothing better which has been put forward; it just gives an indication, but you know if some of us who were perhaps interested in grease-making would leave out of its composition some of these nasty, cheap, easily oxidizable things, then there would be less need for the bomb.

If you remember my Presidential Address * a year ago, when I dealt with greases, I did it with a certain objective : I wanted to focus attention upon the need for really serious thinking on grease. Whether it has had that effect or not I do not know, but there is some good work being done, although unfortunately grease-making is still almost a culinary art.

With regard to the pressure viscometer, I well remember twenty years ago this Institute considering very seriously the pressure viscometer for

* *J. Inst. Petrol.*, 1950, **36**, 367–77.

grease. It never got very far, but I remember Lee, who used to be with the Silvertown company, had a lot to say about it, and then we had an enthusiast from Farnborough, I remember. There has been quite a bit done. I think a great deal of the need for the flow of grease is in ball bearings. I firmly believe, from experiments which have come under my ken, that when grease is once filled into a ball bearing and that ball bearing begins to revolve it does not stay there for many seconds. The quantity of grease which is actually in the bearing when the ball is revolving is extremely small—probably no more than 5 g on a biggish bearing at any one time—but when it stops revolving then the grease flows in, and as you know, the ball-bearing people adjudicate on a grease by the maximum temperature which it goes to. If it goes up and stays up they say that grease is no good, but the point is it probably has not just got the flow properties.

E. G. Ellis: The Hoffmann bomb test was an American invention. It was originally used, I believe, because of a problem which arose in the deterioration of grease in pre-packed bearings: bearings which were stored for some considerable time. To overcome this deterioration the natural development was to include in the make-up of the grease an antoxidant, and the bomb test was a measure of the excellence or otherwise of the inhibitor.

The amount of work which has been done on the flow properties of grease is large and dates back to early days. At the present moment another American instrument has been adopted by the ASTM; that is the SOD pressure viscometer, and there is a likelihood, as it has already entered into certain specifications, that it will have to be considered in due course as a possible standard instrument in the U.K.

D. L. Samuel: The objection which Mr Thomas has raised to the bomb test could be raised against the majority of the tests that we carry out on petroleum products, because many of them have little relationship to performance. You might just as well say: "What does the carbon value tell you?" There are a number of tests open to this criticism, and I do not think it is a valid objection to a test that it does not measure performance. The Hoffmann bomb test is an accelerated oxidation test, and as we know there are a number of these.

B. H. Moerbeek: May I raise the point of still better co-operation between ASTM and IP?

I may be accused, as the Dutch proverb says, of kicking at open doors, but a few days ago I ran into a very striking example of differences between ASTM and IP methods.

Unfortunately, it is an example in the gasoline field, and it might be held that this subject is out of order for this meeting. It is that the ASTM method for the determination of induction period of gasoline uses a better criterion for breakpoint than the IP method, but a combination of the two criteria gives best results. If ASTM and IP had combined their methods some real technical improvement would have been obtained.

I can quote many other cases where is it unfortunate that there is a difference between the two methods. It is rather confusing to the world oil industry that this is the case.

THE CHAIRMAN: In October, 1949, I went to San Francisco at the invitation of the ASTM on a goodwill visit; a few months later Mr Hyams went out to Detroit to a meeting of Committee D.2, and last November Mr Rosen from America came to this very building and brought us greetings and an urge to push on with co-operation. Now it may interest you to know that the President has formed a Technical Committee which is discussing the detail of the definite approach between the IP and the ASTM. At the end of May we have some American friends coming from the United States, and we are arranging a meeting of the Standardization Committee to have discussions with them, so the subject is being very well cared for, I can assure you.

Now I would like to say that the papers which have been presented this evening do not contain any eccentricity of language simply to attract attention. They are written in simple, everyday prose so that the subject matter can be followed by people whose acquaintance with it is not necessarily specialized. Nevertheless, they have manifested a shrewd and penetrating line of reasoning, experiment, and application in their respective fields of inquiry. Every endeavour has been made to avoid a clash with the work of the Standardization Committee by hasty judgments and the inclusion of tests in which standard methods have not been extensively tried out. It is the formal pressure of business which makes much of our testing necessary; therefore it must be as rapid as possible, precise and accurate, and bring peace of mind.

I can assure you that the chairmen of the sub-committees who have presented papers to-night have gone to a lot of trouble in preparing these reports. They are men of undoubted ability, far-seeing, and respected in the industry. We are very fortunate to have men of this calibre to help us in this co-operative work, and we owe them a hearty vote of thanks for the work which they have done for us this evening, also for the work which they have been doing for some years past.

I should like also to say how much we are indebted to Mr Thomas for this very lucid report which he as given us of these four papers. Although perhaps the questions or the criticisms which have been made this evening are relatively few, I do feel that we have done a useful job. We have given you the opportunity of asking questions or criticizing; we may perhaps have educated you in some lines which were not familiar, but in any case I do commend these standard methods and the great work which is being done.

In conclusion, I would like formally to record a very hearty vote of thanks to the four authors—Mr Jagger, Mr Gardner, Dr Garner, and Mr Ellis—and I should like also to associate with them Mr Thomas, and I ask you to carry it in the usual way.

The vote of thanks was carried with acclamation, and the proceedings then terminated.

WATER IN TRANSFORMER OIL—A CRITICAL RÉSUMÉ OF THE CAUSES AND EFFECTS OF WATER IN OIL-FILLED TRANSFORMERS*

By M. R. Dickson

Summary

Consideration is given in this report to the formation of water in transformers and the abstraction of water from the air. The effects of this water on the insulating properties of the oil and the operation of the transformer are also reviewed.

Introduction

The presence of water in an oil-immersed transformer is generally, and rightly, regarded with disfavour. It is not, however, right to suppose that a transformer necessarily gives any trouble when even quite large quantities of water are present. It is hoped that the present brief report will help to clarify this apparent anomaly and put the formation and effects of water in transformers in correct perspective.

Causes of Water in Transformers

Moisture appearing in transformers may have been introduced in three ways: by accidental leakage of water from outside, by chemical reactions in the oil, or by absorption of water vapour from the atmosphere. Of these, the first needs little comment save that in all probability most cases in which free liquid water is found in quantity in the tank must be due to this cause. In such a case the oil would also be more or less saturated with water, with the effects associated with water in solution. The other two cases need further consideration.

Chemical Water Formation

Transformer oil excluded from all contact with oxygen or air is stable for an indefinite period at the temperatures found in transformers. It is, however, liable to oxidation when oxygen is available; under the head of "oxidation" must also be included reactions which, while themselves not involving oxygen, cannot occur without the presence of initial oxidation products. It is not proposed to attempt any summary of the oxidation reactions; such information is given in many papers, for example, references 13, 33, and 39. However, examination shows that in practically every oil-oxidation reaction, water is formed as one product. Other products are acids, often of low molecular weight and partly volatile, and sludges, which are of high molecular weight and formed by polymerization or condensation. Condensation also involves the chemical formation of water.

Several investigators have verified that water accounts for a large part of the oxygen used in oxidation reactions. The results of Muller's investigations [18] are summarized in Fig. 1, which shows the products of oxidation of an over-refined oil at 110° C without catalyst. In addition to the pro-

* Reprinted from *E.R.A. Report Ref.* Q/T126.

ducts shown, gaseous hydrocarbons were formed in amount about equal to the carbon dioxide; small quantities of carbon monoxide were also produced. It can be seen that more oxygen was used to form water than to form any other product.

Muller in the above-mentioned paper concluded that the chemical nature of oxidation is the same for all mineral oils, whatever their origin or treatment; accordingly, it is justifiable to quote Dornte and Ferguson's results,[19, 20] which were obtained using a lubricating oil at 175° C and one atmosphere of oxygen. The formation rates were relatively very much

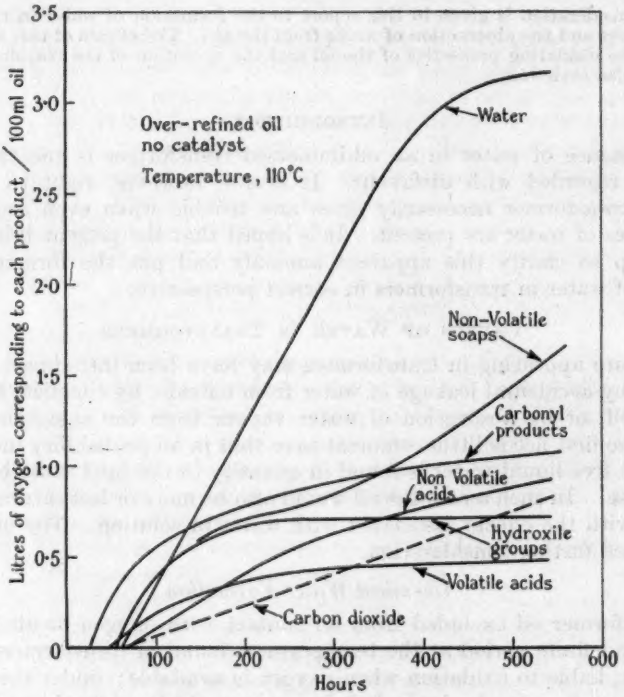

FIG. 1. OXIDATION PRODUCTS AFTER MULLER.

slower than for Muller's oil, as would indeed be expected from the nature of the oil used; the relative amounts of CO_2 and H_2O formed were, however, about the same. The oxygen used in forming water accounted for nearly half the total oxygen absorbed.

Balsbaugh and others [25] also did some tests on this subject. They published no full results, merely stating: "a series of oxidized oils were examined quantitatively for acid, ester, peroxide, and water content. Previous experiments had shown that the amount of carbon dioxide formed was small and that no sufficiently sensitive test for alcohols in the presence of other products of oxidation could be found. These experiments show that water is one of the most important products of oxidation in respect of the quantity produced."

Catalysis and Rates of Formation

Catalysis plays an important part in the oxidation of oil, thus affecting the rates of chemical water formation. It is well established that heavy metals immersed in oils appear to act as catalysts in their oxidation. A certain amount of this action may be a surface catalysis, but it mostly appears to be a chemical action, as follows. Very small quantities of the oil first oxidize, forming minute quantities of organic acids; this oxidation is the same as would occur in the absence of any catalyst or other body, the rate being dependent on oxygen available, temperature, etc. These oxidation products react with the metal or with its oxide, and compounds such as metal soaps or salts are formed, which, dissolving in the oil, are very effective catalysts in both the formation and decomposition of hydroperoxides. Recent work has suggested that, in contrast with the generally held theories regarding the activity of copper, the metal itself does not react, but that the cuprous oxide always present combines with acids formed by oxidation to form catalytic copper salts.[46] The whole oxidation rate is gradually speeded up by the accumulation of catalyst formed in this way; below certain catalyst concentrations, it has been shown that the rate of oxidation is proportional to the amount of catalyst present. At higher concentrations it has been found that the oxidation rate is independent of catalyst concentration; thus, after oxidation has proceeded for some time, the oxidation rate becomes constant. Recent evident of the nature of the catalytic process is quoted by Beaven, Irving, and Thompson,[50] and experimental verification of the various steps has been found by Vellinger and Muller,[16] who showed the initial increase of oxidation rate (judged, unfortunately, by sludge deposition only) settling down to a constant rate after a time; results given by Pollitt [33] and by Hurworth [42] can also be similarly interpreted. Results given by George, Rideal, and Robertson [39] and by Vellinger and Muller [16] show the proportionality between oxidation rate and catalyst concentration, and the independence of rate above certain concentrations.

Kreulen and Ter Horst [30] have published another theory, that only in a short initial period does the catalyst have any effect. The action of the metal is thought to be to absorb antioxidants in the oil, after which oxidation is free to proceed. (This theory is supported by the observation that the oxidation rate of over-refined oils is not greatly affected by catalysts, if it be assumed that over-refining effects removal of anti-oxidants in the oil.) There is, however, no doubt that metal soaps do act as catalysts, for tests have been made using these substances alone as catalysts.[16, 18, 25, 48, 50, 51] It seems possible that both actions occur; the latter applying initially, after which the former action operates. Metallic soaps have been found on windings; they have limited solubility in oil, so after a time are deposited along with other sludges. It seems most likely that minute quantities of these catalytic substances, left on parts of a transformer by imperfect cleansing when oil is changed after oxidation of a previous filling, are responsible for the often observed rapid oxidation of the new oil.[28, 34, 35]

Comparison of the catalytic activity of various metals (or their derivatives) is made rather difficult in some cases owing to conflicting results and

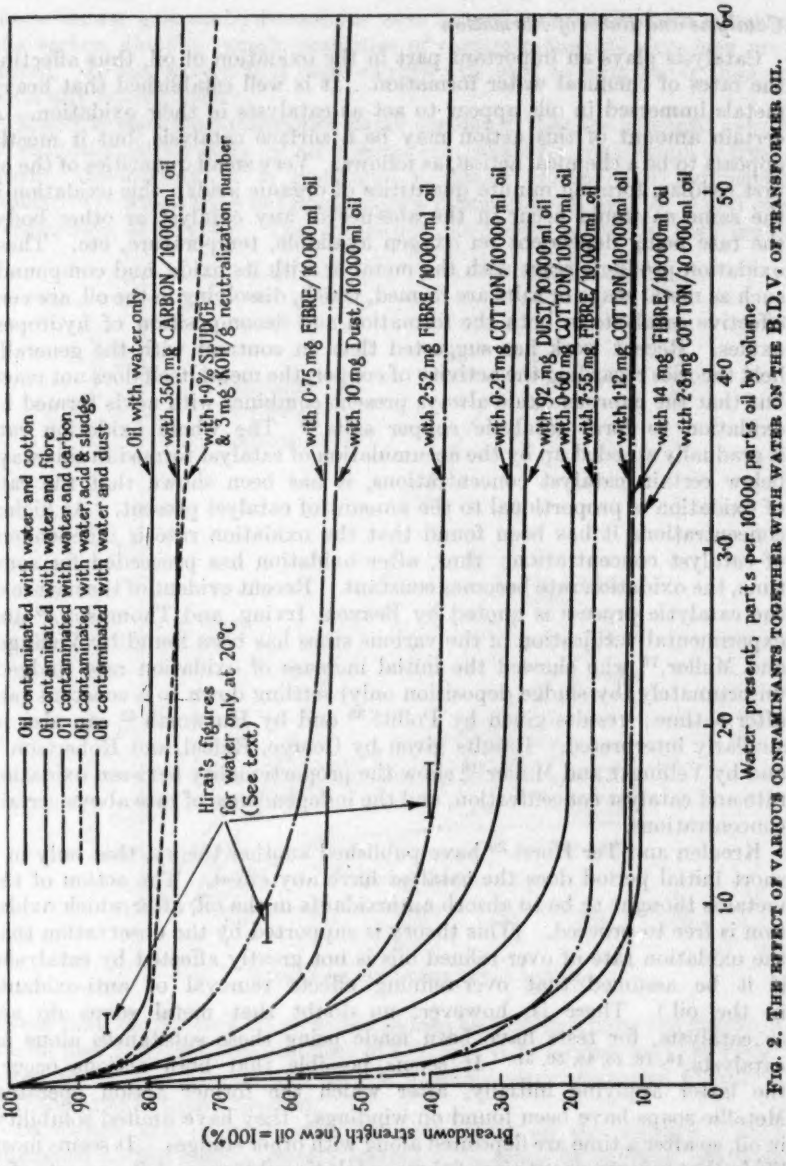

FIG. 2. THE EFFECT OF VARIOUS CONTAMINANTS TOGETHER WITH WATER ON THE B.D.V. OF TRANSFORMER OIL.

to lack of evidence. There is no doubt, however, that copper is the most active metal in this respect; the activity of copper oxide is about 70 per cent that of copper. Iron or steel is stated [32] to be fairly active (about 30 per cent as active as copper), although in view of the large amount of ferrous metals used unprotected in transformers without any obvious action, this may be open to doubt. About lead, opinions vary: Beckin-

sale's [32] figures indicate no effect; Dornte and Ferguson [20] observed slight catalysis; while both Salomon [17] and Sommerman [23] observed considerable activity, the latter's figures indicating about 50 per cent the activity of copper. Reports have been received of lead washers being attacked when used in transformers, with the formation of lead soaps; such action, being analogous to the action with other metals, leads to a strong presumption of catalytic activity. It would appear that lead is best avoided if possible. Tin is stated by two authors [20, 32] to have little or no activity; this inertness extends to tin-coated copper, and is not appreciably affected by scratches in the coating exposing a small area of copper. No information is available on the activity of solder, but since this contains about 50 per cent of lead it

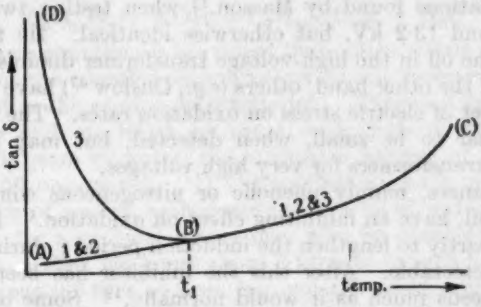

FIG. 3. THE LOSSES IN OIL AS AFFECTED BY MOISTURE CONTENT AND TEMPERATURE (AFTER BAREL). 1. DRY OIL; 2. WET, UNSATURATED OIL; 3. WET, OVER-SATURATED OIL.

would appear to be desirable to protect a soldered joint under oil by a varnish or other coating. Other metals having moderate activity are aluminium, nickel, and cadmium.[32]

Other substances also appear to act as catalysts. Some types of glass seem to be a trifle active; [13, 45] Coursey and Trencham [37] suggest that dust may have catalytic effects. The field opened up would appear enormous; not only various types of varnish, for example, but also traces of substances in tapes, papers, etc., could easily affect oxidation.[52]

Muller [18] observes that for over-refined oils (presumably roughly corresponding to the pre-war grade A) the addition of a catalyst (in this case copper stearate) had little effect on the oxidation rate, but some effect on the induction period. This observation is also supported by Pollitt's [23] figures (cf. his curves for grade A oil in his Figs. 2 and 3). The behaviour of several types of transformer oils, with both inhibitor and catalyst added, is dealt with in a paper by Beaven, Irving, and Thompson.[50]

Salomon's tests [17] showed that a suitable varnish has no catalytic effect on oil oxidation; on the contrary, by keeping a catalytically active metal from contact with the oil, it is beneficial.

The speed of oxidation, in common with most chemical changes, increases rapidly with a rise of temperature, an increase of 10° C doubling or trebling the reaction rate: thus effective oil cooling is necessary at all times if deterioration is not to be rapid.

Hurworth [42] has suggested, and supported his suggestion by experiment, that sludge and other oxidation products may be formed very much more

readily in the oil vapour held above the oil surface, under the action of electric fields present. While no specific mention is made of water formation, if the reactions are substantially the same as occur in the body of the oil, water would be formed; some no doubt would escape as vapour, if ventilation is provided, but some would condense and contaminate the oil. This acceleration (an acceleration of several thousand times is said to be quite likely) might possibly give a clue in mysterious cases of formation of water or other oxidation products; for example, the oil level may have fallen, giving high electric stresses.

Some workers [5, 14, 24, 41] have found evidence of acceleration of oxidation by electric fields in the oil. This may also have been the cause of the oil-resistivity variations found by Masson,[11] when testing two transformers wound for 5 and 13·2 kV, but otherwise identical. He found that the resistivity of the oil in the high-voltage transformer diminished more than the other. On the other hand, others (*e.g.*, Onslow [37]) have been unable to detect any effect of electric stress on oxidation rates. The effect would in any case appear to be small, when detected, but may possibly be of importance in transformers for very high voltages.

Other substances, mainly phenolic or nitrogeneous compounds, when added to the oil, have an inhibiting effect on oxidation.[1] It appears that their effect is partly to lengthen the induction period : during this time no oxidation is detectable. After this the inhibitor has been used up and oxidation proceeds much as it would normally.[18] Some other materials, known as retarders, slow down the oxidation rate : for example, Dornte and Ferguson [20] state that water and carbon dioxide, both products of oxidation, retard the reaction.

In the presence of powerful catalysts such as copper (or rather the products formed from copper), some inhibitors are totally or partially ineffective.

Quantities of Water Formed

It is of interest to arrive at an estimate of the quantity of water produced from the oil by chemical means. It must be realized that such a figure bears a direct relation to the quantity of water found in practice only in the case of a completely sealed transformer or a conservator transformer; in other cases it is certain that a very large proportion of water formed is normally evaporated and passes out of the transformer, because the oil operates at temperatures approaching 100° C. The proportion thus lost must vary widely with the operating temperature, operating cycles, and degree of ventilation.

The oxidation of oil leading to acid formation is a chain reaction, in each stage of which water is produced; thus the acidity value of the oil is directly related to the quantity of water formed by the complete chain reaction. A figure calculated on this basis for the quantity of water formed is a minimum figure, since the chain reaction proceeds to completion for only a proportion of the total oil molecules affected. Also, in practice oxidation reactions occur other than those given below, and these also lead to water formation but do not affect the acid value. For example, carbon dioxide is invariably formed, reducing the number of carbon atoms in the affected molecules and involving the formation of water; also condensation

usually occurs between intermediate products of the oxidation chain reaction, giving water as a further product. A calculated figure is useful, however, since it indicates the order of magnitude of the quantity of water produced.

Consider as an example an oil consisting entirely of paraffinic hydrocarbons, C_nH_{2n+2}, part of which oxidizes to organic acids. The overall reaction may be represented by :

$$2C_nH_{2n+2} + 3O_2 = 2C_nH_{2n}O_2 + 2H_2O$$

the products formed being, in this case, fatty acids and water. In testing for acidity of the oil, these acids are neutralized with potassium hydroxide to form the normal salts :

$$C_nH_{2n}O_2 + KOH = C_nH_{2n-1}O_2K + H_2O$$

From these two equations it is evident that one molecule of water formed by oxidation of the paraffins is equivalent to one molecule of potassium hydroxide used in the acidity determination. Thus if a sample of this oil had an acidity of 1 mg KOH per gram, each gram of oil would contain $18/(56 \times 1{,}000)$ gram of water, the molecular weights of H_2O and KOH being 18 and 56 respectively. It follows that for each gallon of oil and each mg KOH/g of acidity, rather more than 1 ml of water is produced.

An estimate for a particular case may also be obtained from Muller's results (Fig. 1). After 300 hours about 2 litres of oxygen had been used to form water, about 0·6 litre to form non-volatile acids, and about 0·4 litre to form volatile acids. At a lower temperature, the division between volatile and non-volatile acids would be different, but the total acid content could not be greater than would correspond to 1·0 litre of oxygen, nor presumably less than would correspond to 0·6 litre. If all the acids produced are assumed to have been monobasic and to have included two atoms of oxygen in each molecule, it followed immediately that between 7 and 12 ml of water were formed in each gallon of oil for each degree of acidity.

The lack of close agreement between these figures and the value of 1 ml/gallon/degree of acidity obtained above is not at all surprising, for the reasons previously stated. The values do show, however, that the quantity of water so formed is quite appreciable, and doubtless the only reason why trouble is not often encountered, even with acid oil, is that the water rapidly evaporates at normal oil temperatures. Cases in which a little water is found in the bottom of the tank (apart from accidental leakage) are possibly due to a load cycle which allows sufficient time between on-load periods for the water to collect in the cool lower parts of the tank. In addition, excessive acidity arises in only a small percentage of the total transformers in operation, particularly when class B oil is used.

Abstraction of Water from Humid Air

It is possible for the water vapour invariably present in the air to be deposited as fluid water in a transformer tank. Usually this is effected by condensation on the inner tank surfaces.

Condensation

In order that condensation on a surface can take place, the surface must be colder than the moisture-bearing air, and below the dew point corre-

sponding to the humidity of the air. Thus it would appear that a freely ventilated transformer under load is immune from condensation troubles. Since the lid receives some heat from the transformer itself, it is likely to be slightly warmer than the air below it, especially if this air is replaced by a flow of cold air from outside. But the same transformer after shut-down and cooling off is very vulnerable to condensation; even the warmth produced by leaving it energized may not be enough to prevent this trouble. When cold, condensation occurs very readily on metal surfaces under favourable atmospheric conditions; usually the mechanism is as follows. After a cold night (or other cold spell) the air begins to be warmed, either by warming of the ground by the sun or by the arrival of a warm air stream. Moisture evaporating from moist ground ensures a high humidity. Metal objects, however, largely by reason of their high thermal capacity, lag behind the air temperature, and in consequence moisture is deposited on them, sometimes in surprisingly large quantities. Deposition of water also naturally occurs when, because of a slow drop in air temperature, the relative humidity reaches 100 per cent.

The water condensed out in such a manner on the inner surfaces forms drops which fall into the oil and settle on the bottom of the tank. A shut-down of a week or two in suitable atmospheric conditions could produce noticeable quantities of water in the bottom of the tank.

Prevention of the trouble is not easy and in a fully ventilated design could be ensured only by maintaining all the internal surfaces at a sufficiently high temperature; this may be inconvenient. Some improvement can be effected by creating a continuous rapid air circulation through the air space. By making the metal surfaces follow air temperature changes more closely, condensation is largely prevented: any moisture that does condense is likely to be evaporated by the air flow, unless the relative humidity is 100 per cent.

Obviously, if the transformer could be completely sealed, no moisture ingress would be possible. Unfortunately, even a very small fault in the tank-lid joint may lead to trouble; the resistance to air flow offered by even very small apertures is small under transformer breathing conditions, due largely to the small air velocity. Thus on cooling, humid air is drawn into a transformer with an imperfect tank-lid joint; the moisture may easily be condensed on to internal surfaces if conditions are favourable. In fact, a transformer with an imperfect " air-tight " joint may be subject to more water deposition than a fully ventilated transformer. In the latter case moisture which is condensed on internal surfaces may be partly evaporated and removed by the slight air currents through the air space.

The only method of ensuring complete absence of trouble would appear to be the use of a specially designed joint using a suitable gasket material, which could be made and re-made several times without becoming faulty. A method of testing the joint after completion and final sealing seems very desirable: the provision of an air valve communicating with the air-space, together with a suitable pressure gauge, would enable moderate air pressure to be applied; observation over a period of time would indicate the presence of a leak. Allowance might have to be made for variations in ambient conditions, depending on the test pressure used.

Another possible method of ensuring an air-tight joint, which does not

require testing whenever made or re-made, is to make the joint between lid and tank below normal oil level. Any faults in the joint then only result in a slight leakage of oil; air cannot readily enter due to the slight head of oil above the joint inside the tank. Such a design is, however, somewhat inconvenient, since it is necessary to remove some of the oil (by the drain valve) before removing the lid; provision of filling valves is also necessary, as in a conservator transformer proper.

Any hermetic seal of the above types introduces its own problems. In both the above schemes taps or valves are provided: these, of course, must be quite air-tight when closed. It would also be desirable that precautions be taken to ensure that they could not inadvertently be left open. The tank design, to ensure that pressure differences between inside and outside cause negligible distortion, should offer no difficulty.

In suitable locations the provision of free breathing with drying of all air admitted ensures no moisture absorption. In this case, a perfect joint is not required, provided it is good enough to prevent air by-passing the breather; the drying agents need to be frequently inspected to make sure they are in good condition, so that isolated transformers are unsuitable for this approach.

Direct Absorption from the Air by the Oil

Apart from possible condensation, oil does, to a certain extent, absorb or dissolve moisture held in the air in contact with it. In the course of time, the oil becomes practically saturated with moisture, if maintained at a steady temperature.

It was thought that the water might possibly be concentrated and deposited near the bottom of the tank by the action of the normal convection currents, as follows. Hot oil dissolves considerably more water than cold oil (see Refs. 6, 27, and the International Critical Tables for similar organic fluids). Thus possibly hot oil at the surface of the transformer in fairly rapid movement, might dissolve water from moist air; the oil and dissolved water descending and being cooled, the tendency is for water to be thrown out of solution. If the oil at the bottom of the tank is stationary or nearly so, in the course of time some quantity of water might settle out as a fluid layer.

To investigate this further, the apparatus described below was constructed. Oil in a tall 800-ml beaker was heated by a central steam coil, and cooled by a concentric but larger cold-water coil. A glass cylinder between the coils ensured suitable convection currents. Spacing was so adjusted that the currents of hot oil passing across the top surface were fairly rapid, while those of cold oil at the bottom were as slow as practicable. The oil temperature was about 80° C at the top, and some 35° to 40° C at the bottom of the apparatus. A layer of anhydrous copper sulphate at the bottom of the beaker served to indicate the presence of free water in the bottom: it was ascertained that it would abstract water even in the presence of oil, and was capable of detecting small quantities easily (0·01 per cent of water by volume was readily detected). A current of cold air which had been passed through two columns of water to ensure a fairly high humidity, was passed over the hot surface. The precise humidity was not considered important, for Masson [6] was of the opinion that the relative

humidity of air had little effect on the rate of moisture absorption by oil, provided that this relative humidity was above about 70 per cent. The passage of the air across the oil surface was fairly rapid, so that the relative humidity was not likely to have been materially reduced by heating of the air.

Operation of this apparatus for over 100 hours, however, showed no change in the copper sulphate. From a knowledge of the amount of water required to affect its colour, it is concluded that practically no fluid water was abstracted from the atmosphere by this means. It may also be concluded that no significant quantities of water are likely to be deposited in an actual transformer in a like manner.

It is possible that a similar action occurs as the oil temperature changes due to alterations of load. The bulk of the oil in a transformer running at about full load is fairly hot and is capable of dissolving some definite small quantity of water from the air. If the load on the transformer were now to be removed or much reduced, the oil temperature would fall considerably, and it is likely that all the water could no longer remain in solution. Water thrown out of solution would, given sufficient time, descend to the bottom of the tank, and since this region remains cool even when the transformer is on load, the water is likely not to be redissolved. Repetition of this process could lead to a significant quantity of water being deposited.

The Effects of Water in Transformers

The oil in a transformer should fulfil two primary purposes; that of removing heat from the windings and core and disposing of it elsewhere, and that of assisting in the insulation of the windings. The cooling qualities of an oil are not directly affected by moisture, so that this function need not be considered : the electrical qualities are, however, often greatly affected by even very small quantities of moisture.

A transformer oil should have a high breakdown strength, so that clearances between windings and earthed metal-work may be kept to a minimum to save both space and oil. Its resistivity should be high, or in other words, its power factor should be low. It should not have any deleterious effects on other parts of the transformer, either under normal or abnormal operating conditions.

It is convenient to consider separately the way in which water alters these properties.

Effects of Water on Breakdown Strength

The effect of water on the B.D.V. of oils has been shown by work done for the E.R.A., and published more fully elsewhere.[3, 4, 7, 8] In these tests, varying small amounts of pure water were added to oil, either alone or in addition to cotton fibres, pressboard fibres, atmospheric dust, finely divided carbon (from arcing), or sludge and acids formed by oxidation. Some of the results obtained have been replotted as Fig. 2, in which breakdown values are given as a percentage of the figures for pure oil. The temperature at which the tests were carried out does not appear to have been controlled : it may reasonably be assumed that room temperatures were used.

It can be seen from these curves that most deterioration in breakdown

strength occurs with the addition of the first small amounts of water (and the same is true of the other contaminants) so that the damage to electrical properties is done almost as soon as any impurities are allowed in the oil. Pure water alone, however, even in quantities greatly in excess of saturation (which is about 0·005 per cent by volume at room temperatures) only reduces the B.D.V. to 80 per cent of its initial figure: it is of interest to note that the curve flattens off near the figure given above for saturation, 0·005 per cent or 0·5 parts per 10,000.

Comparison with Hirai's figures, for contamination with water alone, shows considerable disagreement with the E.R.A.'s values (see plotted points in figure), his results indicating much lower breakdown strengths. This might conceivably be due to a different type of oil, but it seems most likely to be due to unnoticed impurities, other than water, in this worker's test oil. The figures given [3] for the B.D.V. of an oil exposed to a humid atmosphere are also lower than would be expected for water alone; it is stated in the report that it was thought other contamination was likely.

Cotton and pressboard fibres alone in the oil (these results are not plotted) again only produced some 20 per cent reduction in B.D.V. But when water is present as well as fibrous matter, the B.D.V. is reduced very considerably and may be brought down to less than 10 per cent of the initial figure. It seems likely that the effect is due to moisture being absorbed by the fibres, which, lining up in the test electric field, effectively reduce the flash-over distance. The tests show that cotton fibres produce a greater effect than pressboard fibre, weight for weight; while this might easily be due to the different nature of the fibres and to the possible presence of residual impregnants from the pressboard, limiting the quantities of water absorbed for a given weight of fibre, the authors state [3] " the difference was probably due to the better method of drying the pressboard fibre before addition to the oil."

Tests showed that ordinary atmospheric dust with water was capable of reducing the B.D.V. considerably, but the quantities required, as can be seen from the figure, are greatly in excess of those of fibre or cotton needed to produce a comparable reduction in electric strength.[7] Since, however, with free breathing there appears to be no limit to the quantity of dust that could in time accumulate, this material may be a definite source of danger.

Other impurities have relatively little effect. Carbon alone causes a drop in B.D.V. of about 15 per cent, and together with water a drop of some 30 per cent, for 350 mg carbon per 10,000 ml of oil. An oil containing a large amount of acidity and sludge with water had the B.D.V. reduced by about 30 per cent.

Thus, so far as the breakdown strength is concerned, while an oil is free from fibrous impurities, moisture excess in considerable quantity has relatively little effect on pure oil or on sludge-, acid-, or carbon-contaminated oil. The drop, some 30 per cent of the new B.D.V., is not likely to be of any practical importance even with a " tight " design in which clearances have been reduced to a minimum. But, when fibres are present a very important drop can occur, which may lead to breakdown. It is rare to have an oil completely free from fibre, which is usually produced from the winding or core insulation in service, so great care must be taken to

keep oil-immersed apparatus dry and the oil free from moisture, to avoid trouble due to the simultaneous presence of fibres and water. Even a small transformer with relatively large clearances may break down from this cause, and it is on such small transformers, which have no conservators and which are allowed to breathe freely, that most trouble is likely to occur from oxidation of the oil. Consequent water, acid, and sludge formation would reduce the oil breakdown strength very considerably. On the other hand, if there is no fibre or dust in the oil, large quantities of water may be present without causing any trouble; alternatively the design clearances may be sufficiently great or the voltages sufficiently low to make breakdown improbable even if the electric strength of the oil is very low.

It is stated in Ref. 1 that the addition of certain anti-oxidants to the oil may reduce the B.D.V. by any amount up to 40 per cent.

As pointed out in Ref. 3 the presence or otherwise of preliminary or pilot sparking appears to have some bearing on the nature of impurities present : to quote this report, " Pilot sparking does not occur in a perfectly dry oil containing dry impurities or in an oil containing water only. There must be water and fibres present before pilot sparking occurs, and it does not always happen even then. The length of the fibres present appears to have some effect, as the phenomenon was more frequent with long than with short fibres." A similar result is reported in Ref. 2.

The breakdown strength of oil, contaminated with water only, increases as the temperature increases. According to Hirai's theory [29] the effect is linked directly with the size of water particle in the oil : water solubility increasing with temperature, the particle size is smaller at higher temperatures than it is at low temperatures. The particles under the influence of an electric field apparently become elliptical, and arranging themselves with the major axes in the field direction, effectively reduce the breakdown length. These water particles are present only when the oil is at or above saturation : under these conditions the effect stated, that of increase of B.D.V. with increase of temperature, occurs. Below saturation the water present is not in the form of droplets, and the effect on B.D.V. with temperature is then small.

Effects of Water on Resistivity and Power Factor

From the operating point of view, the resistivity of an oil in a transformer is of practically no importance. Values are so high, even for the poorest oils, that losses due to leakage currents can amount only to a watt or two. In a cable or condenser, where the oil is more or less stagnant, high power factor or low resistivity may produce local concentrations of dielectric loss, leading to instability and possibly to eventual breakdown, but transformer oil continuously circulating is hardly liable to such deterioration. Forrest (reply to discussion, Ref. 44) said he could not cite any cases of trouble arising from low resistivity of a transformer oil.

The resistivity of an oil does, however, assist in estimating the general condition of an oil, *i.e.*, whether oxidized or not, and whether free from contamination. Oxidation, as pointed out in Section (2), invariably produces water by chemical action, and water can often be detected by resistivity measurements. In addition, other products of deterioration also appear to be instrumental in reducing resistivity.

The D.C. resistivity measurements may for most purposes be linked with the power factor of the oil.[10, 32, 43] The dielectric absorption of an oil, and other loss components associated with its A.C. behaviour, may generally be neglected unless the oil is in good condition: this good condition is shown very well by a D.C. test.

Borel [27] showed that the resistivity of an oil in which water is dissolved completely (*i.e.*, containing up to some 0·004 per cent of water around 20° C) is for all practical purposes indistinguishable from the resistivity of a pure oil. Only when free water is present (usually in the form of minute droplets leading to a cloudiness of the oil) is the resistivity reduced; the reduction is considerable. This result is confirmed by measurements on power factor; Gillies and Black [21] showed that allowing oil over-saturated with water to stand for several days caused a progressive decrease of power factor, until the value for new oil was eventually reached: that is, the water droplets settled out leaving only the dissolved water, which did not affect the resistivity.

From these experiments it may be inferred that water is not dissociated when dissolved in the oil, but that free water present in oil is dissociated, much as if the oil was not present. Although pure water is normally dissociated to only a very small extent, this is enough to give a conductivity many times greater than for oil. For example, the conductivity of oil is of the order of 10^{-15} mhos/cm [22, 27] and for pure water, 4×10^{-8} mhos/cm.

Since more water dissolves in hot than in cold oil, raising the temperature of an oil containing only water may profoundly affect the resistivity, if this temperature alteration causes all the water to pass into solution. The effect is then as shown in Fig. 3 (after Borel). Dry oil (curve 1) and oil with insufficient water to become saturated over the experimental range (curve 2) follow the same loss curve ABC. Oil oversaturated at low temperatures (curve 3) has very high losses at low temperatures (D); raising the temperature reduces the losses until at t, all water is in solution and the loss curve from B onward is the same as curves 1 and 2. The action is reversible: on reduction of temperature the curves are retraced.

It would appear that other oxidation products affect the resistivity very considerably, and that in using resistivity measurements to examine the condition of an oil these products must be considered. This aspect is outside the scope of the present report, but to name only a few, papers have been given by Masson [9, 11]; Whitehead,[10] who shows the effects of metal soaps on conductivity; Gillies and Black,[21] who give figures for the power factors of artificially oxidized oils; Beckinsale,[32] who gives resistivity and loss figures for many types of oil at various temperatures; Thompson and Wood-Mallock,[36] who give further figures for metal-soap-contaminated oils; and Forrest,[43] who describes test equipment and gives resistivity figures for samples of oils deteriorated in service.

Other Effects of Water

Water in a transformer may affect it in two other main ways. Water present in the oil is readily absorbed by paper or other absorbent insulation: Walmsley [44] states: "An experimental investigation showed that immersed fibrous insulation had considerable moisture regain owing to the transference of the water vapour of the atmosphere through the oil. This

tends to emphasize the need for the correct selection of fibrous insulating materials and of ensuring they are treated or finished by processes and coatings which provide adequate protection. The need for such precautions obviously increases when onerous conditions obtain such as those found in the gear in which the oil is normally cold." The insulation affected may be seriously damaged by water passing into it by osmosis; in addition, its electric strength would be seriously impaired, leading to a number of troubles such as tracking, burning of the insulation, or electrolysis leading to gas formation.

Water present in the oil, and more especially water vapour in the space above the oil, may lead to corrosion of steelwork, and possibly attack of non-ferrous metals. Corrosion above the oil occurs chiefly when a transformer is heavily loaded so that it runs at a high average temperature; conditions for acidity and water development are then good, and the mixing of volatile acids, oxygen from the air, and condensed water would seem to provide good conditions for the mixed chemical and electrolytic actions which go towards the complicated processes of corrosion. This subject is, however, considered in Ref. 49.

Acknowledgment

The author wishes to thank the Director of the Electrical Research Association for permission to publish the paper.

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THE REACTION OF DINITROGEN TRI- AND TETR-OXIDES WITH OLEFINS. 2-ETHYLBUT-1-ENE AND DEC-1-ENE

By C. R. Porter and B. Wood

Summary

Liquid phase reactions of dinitrogen tri- and tetr-oxides to 2-ethylbut-1-ene and dec-1-ene have been investigated to determine whether these reagents are suitable for characterization of olefins. Tetroxide addition occurred in only two ways, namely, (i) dinitro addition to give 1 : 2-dinitro-paraffins, and (ii) nitro-nitrite addition to give after hydrolysis 1 : 2-nitro-alcohols; both modes of addition occurring in approximately equal extent. In the case of dec-1-ene, however, it was not possible to separate the products completely.

Addition of trioxide to dec-1-ene gave a small yield (3·3%) of a crystalline bis(1-nitro-2-nitroso)-compound together with unstable liquid products, whilst addition to 2-ethylbut-1-ene gave only liquid products identified in part (47%) as the 1 : 2-nitro-alcohol and dinitro-compound.

Periodate oxidation of the 1 : 2-amino-alcohol and diamine derived from 2-ethylbut-1-ene proceeded in analogous manner to that of α-glycols to yield ammonia and carbonyl fragments, identification of which located the original position of the double bond. For both oxidations the optimum pH was 8, that of the amino-alcohol being rapid (1 hour) and quantitative, whilst that of the diamine was much slower and not quantitative.

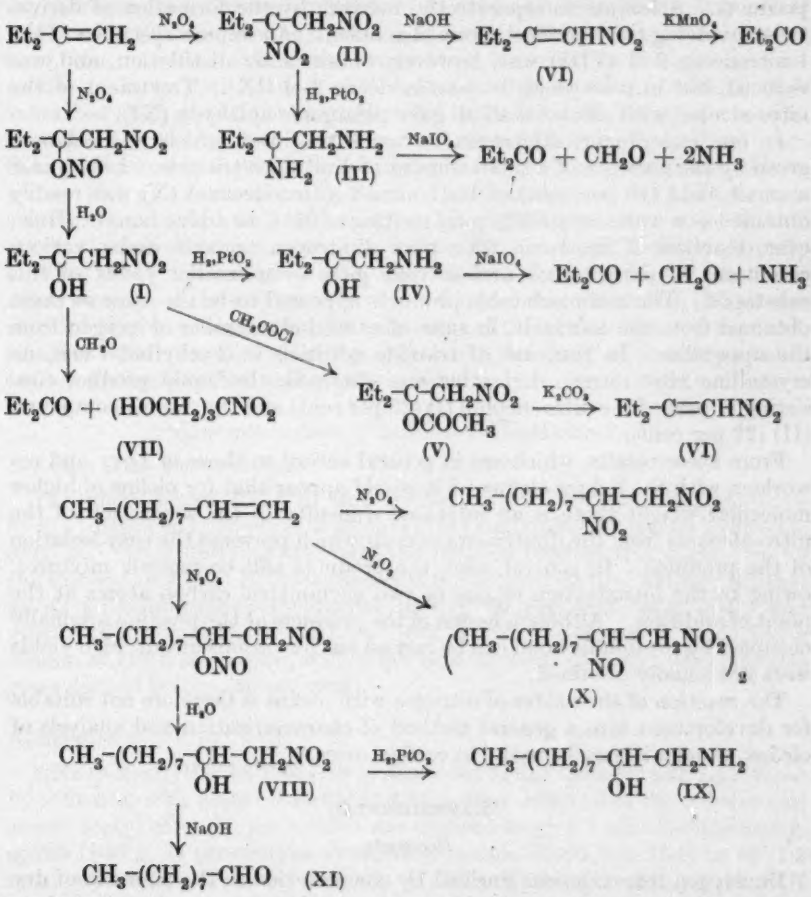
Reactions of olefins with nitrogen oxides have been examined as a means of characterizing, and of determining the positions of double bonds in olefins.

Much of the early work on the reactions between olefins and oxides of nitrogen was vitiated by the use of unpurified mixtures of nitrogen oxides. However, the work of Levy and his co-workers [1,2] showed that by the addition of pure dinitrogen tetroxide to the lower-molecular-weight olefins, it was possible to obtain good yields of mixtures of the corresponding dinitro-paraffins and nitro-nitrites, the latter being readily hydrolysed to the much less unstable nitro-alcohols. It was thought that higher-molecular-weight compounds in this series might possibly be crystalline, and serve for ready characterization of the olefins; and further, that means might be found to split these nitrogen compounds to give approximately quantitative yields of fission products which would show the positions of the double bonds.

The present work describes the products formed by the addition of dinitrogen tri- and tetr-oxides to 2-ethylbut-1-ene and dec-1-ene, the principal reactions investigated being outlined in the scheme on p. 389.

From the reaction of dinitrogen tetroxide and 2-ethylbut-1-ene there was obtained a mixture of 1-nitro-2-ethylbutan-2-ol (formula I) and 1 : 2-dinitro-2-ethylbutane (II). These two compounds could be readily separated by reason of the solubility of the alcohol in water. Hydrolytic fission of the nitro-alcohol by dilute aqueous alkali gives diethyl ketone, whilst fission by alcoholic alkali in the presence of formaldehyde gives diethyl ketone and nitrotri-(hydroxymethyl)methane (VII). In neither

case, however, were the yields quantitative. Attempts to prepare derivatives by utilization of the hydroxyl group gave either liquid (*e.g.*, acetate (V)) or tarry products. Treatment of the acetate with anhydrous potassium carbonate gave an unsaturated nitro-compound (presumably 1-nitro-2-2-ethylbut-1-ene (VI)), which on oxidation with aqueous permanganate gave diethyl ketone. Tarry products were also obtained, together with some ammonia, on attempting to reduce the nitro-alcohol by any of the usual processes, with the exception of catalytic hydrogenation in dilute glacial acetic acid solution over Adams's platinum catalyst. The liquid 1-amino-2-ethylbutan-2-ol (IV) obtained by the latter method gave a crystalline benzoyl derivative and hydrochloride, and could be quantitatively oxidized by periodate to yield formaldehyde, diethyl ketone, and ammonia.



The dinitro compound on treatment with aqueous alkali formed an unsaturated nitro-compound (presumably 1-nitro-2-ethylbut-1-ene), which on oxidation with permanganate gave diethyl ketone. Reduction of the

dinitroethylbutane under similar conditions to those of the nitro-alcohol gave 1 : 2-diamino-2-ethylbutane (III). Periodate oxidation of the diamine to formaldehyde, diethyl ketone, and ammonia was much slower than that of the amino-alcohol, and consequently further oxidation occurred so that a quantitative yield of formaldehyde could not be obtained. In this respect the diamine behaved similarly to ethylene diamine and propylene diamine, the oxidation of which by periodate was examined for comparison.

Attempts to carry out a similar series of reactions commencing with 1-decene were less successful. Apparently the reaction with dinitrogen tetroxide followed a similar course, but the nitro-alcohol was not soluble in water, and other methods of separation proved inadequate to provide pure products. Attempts to separate the mixture by the formation of derivatives involving the hydroxyl group also failed. An impure specimen of the 1-nitrodecan-2-ol (VIII) was, however, obtained by distillation, and was reduced, but in poor yield, to 1-aminodecan-2-ol (IX). Treatment of the nitro-alcohol with alcoholic alkali gave pelargonic aldehyde (XI).

In one experiment, dinitrogen tetroxide was used which was coloured green by the presence of a small amount of dinitrogen trioxide. In this case a small yield (10 per cent) of bis(1-nitro-2-nitrosodecane) (X) was readily obtained as a white crystalline solid melting at 98° C to a blue liquid. However, reaction of dec-1-ene with pure dinitrogen trioxide under various conditions of temperature and solvent gave even smaller yields of this substance. The main isolatable products appeared to be the same as those obtained from the tetroxide, in spite of careful elimination of oxygen from the apparatus. In the case of trioxide addition to 2-ethylbut-1-ene, no crystalline nitro-nitroso derivative was obtained, the liquid product consisting in part of the nitro-alcohol (I) (25 per cent) and the dinitro-compound (II) (22 per cent).

From these results, which are in general accord to those of Levy and coworkers with the lighter olefins,[1, 2] it would appear that for olefins of higher molecular weight there is an increased difficulty in the separation of the nitro-alcohols from the dinitro-compounds which prevents the easy isolation of the products. In general, also, the products will be racemic mixtures, owing to the introduction of one or two asymmetric carbon atoms at the point of addition. Although fission of the products at the position originally occupied by the double bond can be carried out by various means, high yields were not usually obtained.

The reaction of the oxides of nitrogen with olefins is therefore not suitable for development into a general method of characterization and analysis of olefins, though it may be useful in certain cases.

Experimental

Reagents

Dinitrogen tetroxide was purified by condensation in the presence of dry oxygen, after passage over phosphorus pentoxide to remove traces of nitric acid. Dinitrogen trioxide was prepared by passing nitric oxide through dinitrogen tetroxide at −10° until no more was absorbed. Nitric oxide was prepared by the addition of concentrated sulphuric acid to a stirred

mixture of sodium nitrite and water, and purified by passage through concentrated sulphuric acid.

The olefins were fractionally distilled through a column packed with Dixon packing (45 plates) and had the following physical properties: 2-ethylbut-1-ene, b.p. 64·3° to 64·4°/750 mm; n_D^{20} 1·3968; dec-1-ene, b.p. 169·7° to 169·8°/760 mm., n_D^{20} 1·4217. The National Bureau of Standards [5] gives: 2-ethylbut-1-ene, b.p. 64·95°/760 mm, n_D^{20} 1·3969, and dec-1-ene, b.p. 170·49°/760 mm, n_D^{20} 1·4214.

Addition of Dinitrogen Tetroxide to 2-Ethylbut-1-ene in the Absence of Oxygen

Dinitrogen tetroxide (20 g, 0·22 moles) was carried by a slow stream of dry nitrogen into a stirred solution of 2-ethylbut-1-ene (16·8 g, 0·2 moles) in dry ether (70 cc) cooled to 0° during 1½ hours. After stirring for a further hour, the reaction mixture was worked up according to the general procedure of Levy and Scaife.[1] The water-soluble fraction, *1-nitro-2-ethylbutan-2-ol* (11·9 g, 40·5 per cent), distilled at 72·5° to 73°/1 mm as a colourless mobile liquid, n_D^{20} 1·453. (Found: C, 49·0; H, 9·2; N, 10·0 per cent. $C_6H_{13}O_3N$ requires C, 48·9; H, 8·9; 9·5 per cent.) The portion insoluble in water (16·3 g) was dissolved in 30 cc of methanol, dried with magnesium sulphate and cooled to −70° to give 7·9 g (22·5 per cent) of solid 1 : 2 *dinitro-2-ethylbutane*, m.p. 14°, b.p. 91° to 92°/1 mm., n_D^{20} 1·461. (Found: C, 40·8; H, 6·9 per cent. $C_6H_{12}O_4N_2$ requires C, 40·9; H, 6·9 per cent.) After removal of the methanol from the filtrate, the residual oil (8·3 g) was distilled to give a further 5 g (14 per cent) of the above dinitro-compound, together with a fraction 1·7 g, b.p. 97° to 103°/1·5 mm; n_D^{20} 1·467 (probably mainly dinitro-paraffin) and a tarry residue.

Characterization of 1-Nitro-2-Ethylbutan-2-ol

Reaction with Formaldehyde

The nitro-alcohol (0·74 g) was treated at 20° with paraformaldehyde (0·45 g) dissolved in 95 per cent alcohol (3 cc) containing potassium hydroxide (0·05 g). After standing overnight the reaction product was worked up by the method of Levy, Baldock, and Scaife [2] to give diethyl ketone, isolated as its 2 : 4-dinitrophenylhydrazone (0·8 g, 60 per cent, m.p. 154°) and nitrotri-(hydroxymethyl) methane (0·2 g, 26·5 per cent, m.p. 156°). Fission of the nitro alcohol with 2 per cent aqueous sodium hydroxide also gives diethyl ketone (40 per cent).

Acetylation

1-Nitro-2-ethylbutan-2-ol (1·5 g) dissolved in dry benzene was acetylated by refluxing with acetyl chloride (2·4 g). After removal of the solvent and excess acetyl chloride, the residue was distilled to give *1-nitro-2-ethylbutyl-2-acetate* (1·37 g, 71 per cent) as a colourless mobile liquid, b.p. 75·5° to 76°/1·5 mm; n_D^{20} 1·443. (Found: C, 50·2; H, 8·2; N, 7·8 per cent. $C_8H_{15}O_4N$ requires C, 50·8; H, 8·0; N, 7·5 per cent.) On treatment with anhydrous potassium carbonate at 75°, the acetate gave an unsaturated nitro compound (presumably 1-nitro-2-ethylbut-1-ene) which was readily oxidized with aqueous permanganate to diethyl ketone (44 per cent).

Reduction to 1-*Amino*-2-*ethylbutan*-2-*ol*

1·23 g of the nitro-alcohol dissolved in 200 cc of glacial acetic acid was reduced at room temperature by hydrogen at 100 atm in the presence of Adams's platinum catalyst (0·05 g). After filtration, the product was concentrated to about 5 cc under reduced pressure, made alkaline with sodium hydroxide, and extracted with ether. Removal of the ether and addition of concentrated hydrochloric acid gave 1-*amino*-2-*ethylbutan*-2-*ol hydrochloride*; recrystallized by addition of ether to its alcoholic solution, m.p. 138° to 139° (0·77 g, 60 per cent). (Found: C, 47·0; H, 10·5; N, 8·8; Cl, 23·2 per cent. $C_6H_{15}ON,HCl$ requires C, 46·9; H, 10·5; N, 9·1; Cl, 23·1 per cent.) Benzoylation of the amino-alcohol gave 2-*ethyl*-2-*hydroxybutyl benzamide*, m.p. 103°, from benzene. (Found: C, 70·7; H, 8·6; N, 6·1 per cent. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·7; N, 6·3 per cent.)

Oxidation of 1-*Amino*-2-*ethylbutan*-2-*ol by Periodate*

Oxidation of the amino alcohol by the method of Fleury and Lange [3] proceeded to completion in 1 hour at pH 8 and room temperature, the calculated amount of periodate being used.

Ammonia was present in the reaction product, and the formaldehyde and diethyl ketone were converted into their 2 : 4-dinitrophenylhydrazones and separated chromatographically on alumina, using a 1 : 24 benzene/80° to 100° petroleum mixture as the eluent. Alternatively, formaldehyde could be isolated in 90 per cent yield as its dimedone derivative.[4]

Characterization of 1 : 2-*Dinitro*-2-*ethylbutane*

Reaction with Alkali

The dinitro compound was converted by treatment with 5 per cent aqueous sodium hydroxide at room temperature to an unsaturated nitro-compound (presumably 1-nitro-2-ethylbut-1-ene) which was oxidized by permanganate to diethyl ketone (40 per cent).

Reduction to 1 : 2-*Diamino*-2-*ethylbutane*

1·4 g of the dinitro compound in glacial acetic acid (200 cc) was reduced in the presence of Adams's catalyst (0·05 g) at 20° and 75 atm of hydrogen for 2 hours. After filtration, the product was saturated with hydrogen chloride and the solution evaporated under reduced pressure at room temperature. The deliquescent syrupy residue could not be induced to crystallize, but on treatment with an excess of saturated aqueous picric acid, 1 : 2-*diamino*-2-*ethylbutane dipicrate* was precipitated (65 per cent). After recrystallization from aqueous acetone, the fine yellow needles melted with decomposition at 220°. (Found: C, 37·9; H, 3·8; N, 19·4 per cent. $C_{18}H_{22}O_{14}N_8$ requires C, 37·6; H, 3·9; N, 19·5 per cent.)

Oxidation of 1 : 2-*Diamino*-2-*ethylbutane by Periodate*

Preliminary experiments having shown that picric acid was not attacked by periodate, the picrate of the diamine was used for oxidation experiments. The optimum pH was found to be 8, but the rate of reaction was only one-

tenth of that of the corresponding amino-alcohol. Under these conditions, the yield of formaldehyde (as its dimedone derivative[4]) was only 70 per cent. Ammonia and diethyl ketone were identified as in the oxidation of the amino-alcohol.

Addition of Dinitrogen Trioxide to 2-Ethylbut-1-ene

To dinitrogen trioxide (21 g, 0·28 moles) and ether (20 cc) stirred to −10° were added dropwise over 40 minutes, 2-ethylbut-1-ene (16·8 g, 0·2 moles) in ether (30 cc). After 1½ hours, the reaction product was worked up as in the case of the tetroxide additions to give a 25 per cent yield of 1-nitro-2-ethylbutan-2-ol, and 20 g of a water-insoluble oil. The latter consisted of 1 : 2 dinitro-2-ethylbutane (39 per cent) together with smaller amounts of lower and higher boiling fractions which were not identified.

Addition of Dinitrogen Tetroxide to Dec-1-ene

The reaction was carried out as in the previous case, using 28 g (0·2 moles) of the olefin and 20 g (0·22 moles) of dinitrogen tetroxide in ether (60 cc) cooled in ice and salt. The aqueous layer obtained after hydrolysis of the nitro-nitrite contained no nitro-alcohol, and the insoluble oil weighed 46·1 g. On distillation of this material at about 1 mm pressure, the temperature gradually rose from 100° to 126°, the main bulk boiling at 122° to 126°; and a tarry residue was left. It was not possible to carry out the distillation at a lower pressure, owing to the slight evolution of gas (oxides of nitrogen) at the boiling temperature. Attempts were made to separate the mixture by chromatographic adsorption on alumina and silica gel, and by solvent partition between diethylene glycol and light petroleum (40° to 60°), but were unsuccessful. Attempts to reduce the mixture in the hope of separating the amines afforded oily or tarry products which gave no crystalline derivatives with the usual reagents for amines. The product boiling at 122° to 126°/1 mm appeared to be impure *1-nitrodecan-2-ol*. (Found: C, 60·3; H, 10·2 per cent. $C_{10}H_{21}O_3N$ requires C, 59·1; H, 10·4 per cent.)

Characterization of 1-Nitrodecan-2-ol

Reduction of 1-Aminodecan-2-ol

Reduction of impure 1-nitrodecan-2-ol as described previously afforded *1-amino-decan-2-ol hydrochloride* as colourless leaflets, m.p. 160° to 165° (6 per cent), which on treatment with aqueous picric acid gave the corresponding picrate, yellow needles from benzene, m.p. 107°. (Found: C, 48·3; H, 6·5; N, 13·5 per cent. $C_{16}H_{26}O_8N_4$ requires C, 47·7; H, 6·5; N, 13·9 per cent.)

Reaction with Alcoholic Alkali

Fission of the nitro-alcohol with 5 per cent alcoholic sodium hydroxide for 1 hour at 50° gave pelargonic aldehyde (13 per cent) characterized as its 2 : 4-dinitrophenyl-hydrazone, m.p. 96° to 97°.

Addition of Dinitrogen Trioxide to Dec-1-ene

When dinitrogen tetroxide containing a small amount of the trioxide was added to dec-1-ene in the absence of oxygen, a white crystalline solid separated from the blue reaction product, and further amounts of this substance could be obtained by cooling and treating with methanol. The total yield was 10 per cent of bis-(nitro-2-nitrosodecane); obtained from chloroform–light petroleum as colourless crystals melting at 98° to a blue liquid, and giving faintly blue solutions. (Found: C, 56·0; H, 9·5; N, 12·8 per cent. $(C_{10}H_{20}O_3N_2)_2$ requires C, 55·5; H, 9·3; N, 13·0 per cent.) Cryoscopic molecular-weight determinations in benzene gave M.W. 335 ($c = 0{\cdot}34$ per cent), 376 ($c = 0{\cdot}88$ per cent), 400 ($c = 0{\cdot}93$ per cent); $C_{20}H_{40}O_6N_4$ requires M.W. = 432. Attempts to reduce the nitro-nitroso-compound in benzene, and glacial acetic acid, over Adams's platinum catalyst or Raney nickel at 100 atm and 20° to 45°, gave only oily products which could not be purified.

(a) *Addition in Diethyl Ether at* −10°

Addition of dec-1-ene (14 g, 0·1 moles) in ether (20 cc) to a solution of trioxide (14 g, 0·18 moles) in ether (30 cc) stirred to −10°, gave on working up the blue reaction mixture as in the tetroxide additions, bis (1-nitro-2-nitrosodecane) (0·06 g, 0·3 per cent) and a yellow water-insoluble oil (20·9 g) n_D^{20} 1·446. The oil, distilled over the range 70° to 130° at about 1 mm pressure with decomposition, and appeared to be of a similar nature to the liquid product obtained from the tetroxide additions.

(b) *Addition in Diethyl Ether at* −70° *in an Atmosphere of Nitrogen*

An addition of dec-1-ene (14 g, 0·1 moles) in ether 25 cc to a solution of trioxide (15 g, 0·2 moles) in ether (50 cc) at −70°, and in an atmosphere of nitrogen was carried out and worked up as in (*a*) to give 00·7 g (0·3 per cent) of XII, together with 21·1 g of a water-insoluble oil of a similar nature to that obtained in (*a*).

(c) *Addition in Acetonitrile at* −10°

After preliminary tests had shown that acetonitrile (dielectric constant $\epsilon_0 = 42{\cdot}0$ compared to $\epsilon_0 = 4{\cdot}68$ for diethyl ether) did not react in the liquid phase with dinitrogen trioxide, an addition of 8 g (0·105 moles) of trioxide in dry acetonitrile to a mixture of dec-1-ene (14 g, 0·1 moles) and acetonitrile (20 cc) stirred to −10° was carried out. On working up the blue reaction mixture as in previous additions, there were obtained 0·71 g (3·3 per cent) of bis-(1-nitro-2-nitrosodecane) and a yellow oil (18·2 g) which appeared to be similar to those afforded by previous additions.

(d) *Addition in Ether at* −10° *in the Presence of Nitric Oxide*

Dinitrogen trioxide (9 g, 0·12 moles) was carried into a stirred and cooled (−10°) solution of dec-1-ene (14 g, 0·1 moles) in ether (42 cc) by a slow stream of nitric oxide during ½ hour. The reaction mixture was then worked up by the usual procedure to give 0·5 g (2·3 per cent) of bis-(1-nitro-2-nitrosodecane), and 18·85 g of a water-insoluble oil, n_D^{20} 1·466, of a similar character to those obtained in earlier additions.

Periodate Oxidation of α-Diamines

The periodate oxidation of 1 : 2-diamino-ethane and propane dihydrochlorides in aqueous solution at room temperature have been studied by the method of Fleury and Lange.[3] At the optimum pH 8, the oxidations proceeded slowly to completion in about 10 hours, the theoretical amount of periodate required by the general equation :—

$$R_1R_2C(NH_2)\text{—}C(NH_2)R_3R_4 + NaIO_4 + H_2O \longrightarrow R_1R_2CO + R_3R_4CO + 2NH_3 + NaIO_3$$

being consumed. Some over-oxidation does, however, occur in both instances. Consequently, the estimated formaldehyde [4] from the oxidation of 1 : 2-diaminoethane was only 57 per cent of theoretical. The products of oxidation were identified as ammonia and formaldehyde in the case of 1 : 2-diaminoethane, and as ammonia, formaldehyde, and acetaldehyde in the case of 1 : 2-diaminopropane.

All temperatures are uncorrected. Analyses were carried out by Dr Weiler and Dr Strauss of Oxford.

ACKNOWLEDGMENTS

The authors' thanks are due to the Institute of Petroleum for financial assistance through the Hydrocarbon Research Committee, to Imperial Chemical Industries Ltd. for an I.C.I. Fellowship to one of them, and to Professor F. H. Garner for helpful advice.

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SUBSTITUTION PRODUCTS OF THE ISOMERIC THIOPHTHENS. THE STRUCTURE OF LIQUID THIOPHTHEN (THIOPHENO-2′:3′:2:3-THIOPHEN)

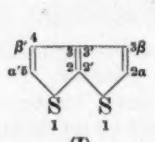
By FREDERICK CHALLENGER * (Fellow) and ROBERT EMMOTT *

SUMMARY

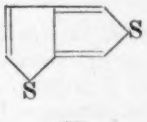
Reductive acetylation of the mono-nitro-derivatives of solid and liquid thiophthen with hydrogen and Raney nickel in acetic anhydride yields two acetylaminothiophthens. These are identical with the products obtained by the Beckmann transformation from the oximes of the corresponding methyl ketones. The nitro- and acetyl-groups therefore enter the same position in the nucleus of liquid thiophthen. This is also true for the solid isomer, but the orientation is not yet known in either case. The hydrochlorides and acetates of the oximes are described. Solid thiophthen gives a mono-iodo-derivative which, on conversion to the Grignard compound and reaction with carbon dioxide, gives a thiophthenoic acid identical with that prepared by oxidation of the methyl ketone (methylthiophthienone). The two methyl esters are also identical. The groups I, $-COCH_3$, $-MgBr$, $-NO_2$, and $-HgO{\cdot}COCH_3$ (see below) therefore enter the same position in solid thiophthen.

The structure of liquid thiophthen is shown to follow from two observations: (*a*) that the nitration of the methyl ketone and the action of acetyl chloride and aluminium chloride on the nitro-thiophthen yield identical nitro-ketones and thence identical oximes; (*b*) that oxidation of the methyl ketone to the carboxylic acid, nitration, and decarboxylation yields the same nitro-compound as is formed by direct nitration of liquid thiophthen.

In a joint communication with Clapham [1] the present authors described several mono-substitution derivatives of the liquid isomer of thiophthen (I) or possibly (II) including iodothiopthen, methyl thiophthienyl ketone $C_6H_3S_2{\cdot}COCH_3$ (methylthiophthienone), the corresponding carboxylic acid $C_6H_3S_2{\cdot}COOH$ and its methyl and *p*-nitrobenzyl esters. The introduction (*a*) of $-COCH_3$ by the Friedel–Crafts reaction, (*b*) of $-MgBr$ followed by $-COOH$ by heating with magnesium ethyl bromide and treatment with carbon dioxide, and (*c*) of iodine, by reaction with the free element and mercuric oxide, was shown to occur in the same position. The orientation was not, however, established. The same was shown by Challenger and Gibson [2] to be true for the solid isomer (III) in the case of reactions (*a*) and (*b*) and of mercuration. With thionaphthen (IV) (*a*) leads to substitution in the 3- or β-position and reaction (*b*) in the 2- or α-position. Further details regarding substitution in thionaphthen are given by Challenger and Miller [3] and Schomaker and Pauling.[4]



(I)



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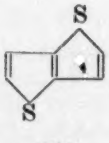

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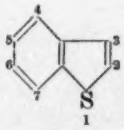
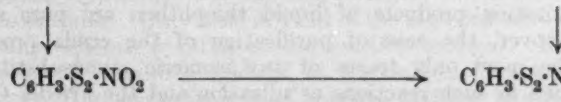


(IV)

* Organic Chemistry Department, The University, Leeds.

It is now found that reductive acetylation of the mono-nitro-derivatives of solid and liquid thiophthen with hydrogen and Raney nickel in acetic anhydride yields two acetylaminothiophthens. These are identical with the products obtained by the Beckmann transformation from the oximes of the corresponding methyl ketones of the two thiophthens.



The nitro- and acetyl-groups therefore enter the same position in the nucleus of liquid thiophthen and also of the solid isomer. Of the various compounds involved in the transformations outlined above, the ketones, oximes and nitro-compounds, and also the acetylamino derivative of liquid thiophthen, have already been described by Challenger and Harrison.[5] The acetylamino-compound of solid thiophthen (*acetylaminothiopheno-2′ : 3′-3 : 2-thiophen*) is, however, new.

The only convenient method for effecting the Beckmann transformation is the action of thionyl chloride on an acetone solution of the ketoximes. The *hydrochlorides* of the two oximes appear to be intermediate products, and can be separated in the early stages of the reaction. They have also been prepared by the action of dry hydrogen chloride on a solution of the ketoxime in chloroform. The *acetates* of the two oximes are obtained by the action of acetyl chloride on the oximes in the absence of a solvent; the hydrochlorides are again intermediate products. No Beckmann change is observed in these reactions.

The iodo-derivative of liquid thiophthen forms a Grignard compound which was shown by Challenger, Clapham, and Emmott [1] to yield, on treatment with acetonitrile, methylthiophthienyl ketone (IL) identical with that obtained by the Friedel–Crafts reaction (KL). The Grignard reagent has now been converted by carbon dioxide to the thiophthenoic acid identical with that obtained on oxidation of the methyl ketone or by the introduction of $-MgBr$ into liquid thiophthen, followed by treatment with carbon dioxide.

Solid thiophthen on treatment with iodine and mercuric oxide yields an unstable mono-iodothiophthen, decomposing within two to three days. The corresponding Grignard compound with carbon dioxide gives a thiophthenoic acid identical with that prepared by oxidation of methylthiophthienone (S). The two methyl esters are also identical.

The groups I, $-COCH_3$ $-MgBr$, $-NO_2$, and $-HgO{\cdot}COCH_3$ (Challenger and Gibson [2]), therefore enter the same position in the molecule of solid thiophthen. The same is true for the liquid isomer, except that its mercuration has not been studied.

The Structure of Liquid Thiophthen

In the communication by Challenger and Harrison [5] it was conclusively proved that the structure of solid thiophthen is thiopheno-2′ : 3′-3 : 2-thiophen (III). Cox, Gillott, and Jeffrey [6] have recently published the results of a complete X-ray analysis of this compound. Challenger,

Clapham, and Emmott [1] showed that the same liquid thiophthen is produced by the action of acetylene on boiling sulphur (when it is accompanied by the solid isomer), as from citric acid and phosphorus trisulphide, when the solid (III) is absent. This question of identity was left undecided in the earlier paper by Challenger and Harrison. The liquid isomer, however, might possibly be represented by either of the structures I or II or conceivably be a mixture of the two.

The monosubstitution products of liquid thiophthen are pure single compounds. Moreover, the ease of purification of the crude products shows that at the most only traces of any isomeric monosubstitution products are formed in such reactions as nitration and the Friedel–Crafts synthesis. Liquid thiophthen itself must therefore be a pure compound represented by (I) or (II), and not a mixture of the two forms. Results now to be described not only substantiate this conclusion, but show that formula (I) is correct.

It will be seen that structure (I) contains two pairs of identical positions, the two α (2 : 5) and the two β (3 : 4), whilst in structure (II) no two positions are similarly situated. Consequently, if two different monosubstituted derivatives of (I) were prepared, the substituents being X and Y, and these two substituents were known to take up the same position in the ring, it might be possible to prepare two disubstituted compounds XY and YX which could be shown to be identical. This would never be possible for structure (II). X and Y should be "deactivating" groups in order that the second substituent should have every facility for entering the second thiophen ring. The nitro- and acetyl-groups fulfil these conditions.

Two specimens of nitro-methylthiophthienone, $CH_3CO{\cdot}C_6H_2{\cdot}S_2(NO_2)$, were prepared (*a*) by the nitration of methylthiophthienyl ketone (LK) and (*b*) from the nitro-derivative of liquid thiophthen by the Friedel–Crafts reaction. They and their oximes were found to be identical by m.p. and mixed m.p. determinations.

Nitroacetothiophthienone (LKN) quickly separated on addition of fuming nitric acid to a warm solution of the ketone in glacial acetic acid. It was re-crystallized from alcohol or acetic acid as yellow needles. No tar or polymer was produced in contradistinction to the behaviour of the two thiophthens on nitration. The oxime formed a red sodium salt.

Nitroacetothiophthienone (LNK) could not be prepared from nitrothiophthen (L) by the Friedel–Crafts reaction using stannic chloride as a catalyst, although this gives excellent results with the unsubstituted thiophthens. Stannic chloride is known to be very mild in its action and to permit of the formation of methylthienyl ketone, but not acetophenone, from a mixture of thiophen, benzene, and acetyl chloride, as was shown by Stadnikow.[7–9] Consequently, the more powerful reagent, aluminium chloride, was employed, when a nitro-ketone (LNK) was obtained which, after crystallization from glacial acetic acid, was indistinguishable by analysis, m.p., and mixed m.p. from the nitro-ketone (LKN). The oximes were also identical. Liquid thiophthen, therefore, contains two pairs of identical positions, and formula (I) is correct.

Treatment of nitroacetothiophthienoxime with thionyl chloride in acetone caused a Beckmann rearrangement giving nitroacetylaminothiophthen as orange, needle-shaped crystals.

The same conclusion as to the structure of liquid thiophthen was reached by further, somewhat analogous experiments. If acetothiophthienone (L) were nitrated and the nitro-ketone oxidized to the nitrothiophthenoic acid, this on decarboxylation should yield a nitrothiophthen identical with that obtained on direct nitration of thiophthen, if formula I is correct.

The oxidation of nitroacetothiophthienone (LK) to the carboxylic acid by sodium hypoiodite was difficult, owing to the insolubility of the nitro-ketone in water. Only a small yield of the required nitro-acid was obtained by using aqueous pyridine as the reaction medium. Hence acetothiophthienone (L), was first oxidized to the carboxylic acid, which was then nitrated. Here again the use of aqueous pyridine in the oxidation was an advantage, an increased yield (75 per cent) being obtained, probably owing to the greater solubility of the ketone in this medium. The pyridine was not attacked. The reaction of ketones with iodine and aqueous pyridine has been studied by King.[10]

The nitrothiophthenoic acid (LK) was prepared by nitration of thiophthenoic acid (LK) with fuming nitric acid in warm acetic anhydride. As some formation of anhydride may occur under these conditions the product was dissolved in alkali and re-precipitated. Its *methyl ester* was also prepared. The attempted decarboxylation of the nitro-acid with soda-lime was unsuccessful, probably owing to extensive decomposition at the high temperature (about 300°) employed. However, on refluxing the nitrothiophthenoic acid in quinoline in presence of copper powder, nitrothiophthen (LK) was obtained in 30 per cent yield.

By m.p. and mixed m.p. determinations this was shown to be identical with the nitrothiophthen obtained by direct nitration of liquid thiophthen, which must therefore contain two identical positions and be represented by structure (I). It has been shown in this paper that $-NO_2$ and $-COCH_3$ enter the nucleus of liquid thiophthen in the same position, a prerequisite for the above argument.

Experimental

Derivatives of Liquid Thiophthen

Conversion of Iodothiophthen (L) to Thiophthenoic acid (LI) through the Grignard Reagent

Iodothiophthen (L) was obtained from liquid thiophthen by the method of Challenger, Clapham, and Emmott.[1] (Found: C, 27·0; H, 1·4; S, 23·7; I, 47·1. $C_6H_3S_2I$ requires C, 27·1; H, 1·15; S, 24·1; I, 47·7 per cent.) The Grignard reagent was prepared from iodothiophthen (0·7 g) and magnesium (0·1 g) in ether (10 cc), by warming; a little dimethylaniline and a crystal of iodine were added as catalysts. Carbon dioxide was passed through the solution for 5 minutes. Acidification gave the crude product; unchanged iodothiophthen was removed by solution of the acid in sodium hydroxide, extraction with light petroleum, and re-acidification. The carboxylic acid on two crystallizations from chloroform gave 0·1 g of constant m.p. 245° (slight decomp). This m.p. was unchanged on recrystallization from water or on admixture with thiophthenoic acid of m.p. 245° (slight decomp) (from oxidation of the methyl ketone). (Found:

C, 46·0; H, 2·5; S, 34·4. $C_7H_4O_2S_2$ requires C, 45·7; H, 2·2; S, 34·8 per cent.)

The methyl ester, m.p. 106·5°, was prepared with ethereal diazomethane. In admixture with the methyl ester of acid (LK) of m.p. 106·5° the m.p. was 106·5°.

Preparation of Acetylaminothiophthen (LK) by the Beckmann transformation on acetothiophthienoxime (L)

Acetothiophthienoxime (L) (1·0 g), m.p. 161°, prepared from the ketone by the method of Challenger and Harrison,[5] was dissolved in acetone (10 cc) and thionyl chloride (0·8 cc) added in one portion with good stirring. After about 10 sec the mixture was poured into water (80 cc) and left for 1 hour. The precipitated acetylaminothiophthen (0·8 g; 80 per cent yield) had m.p. 210° (decomp), and was crystallized to constant m.p. 221·5° from ethyl alcohol, with addition of decolourizing charcoal. The m.p. was unchanged on recrystallization from methyl alcohol. Acetylaminothiophthen (LK) forms colourless rhombic crystals. (Found : C, 48·7; H, 4·0; N, 7·1. $C_8H_7ONS_2$ requires C, 48·7; H, 3·5; N, 7·1 per cent.)

Acetothiophthienoxime (L) Acetate and Hydrochloride

Acetyl chloride (5 cc) was added to the oxime (0·8 g) of m.p. 161°. Hydrogen chloride was at once evolved, and a colourless solid (shown later to be the hydrochloride of the oxime) separated. The mixture was then boiled under reflux for 20 minutes, giving a clear solution. This deposited no solid on cooling. It was evaporated to dryness, and the residue (0·8 g), m.p. 103° to 105°, recrystallized twice from ethyl acetate giving 0·2 g of large colourless plates of constant m.p. 105° having an odour resembling phenyl acetate. It is slowly hydrolysed to the oxime by hot water, very slowly by hot ethyl alcohol, and readily by warm dilute sodium hydroxide; careful acidification gave the oxime, m.p. 161°; warming the acid solution gave the methyl ketone, m.p. and mixed m.p. 117° (Challenger, Clapham, and Emmott [1]). (Found : C, 50·1; H, 4·0; N, 5·87; S, 26·8. $C_{10}H_9O_2NS_2$ requires C, 50·2; H, 3·77; N, 6·0; S, 26·8 per cent.)

The oxime hydrochloride, m.p. 163° (decomp) on slow heating, and 169° to 172° (decomp) on rapid heating was readily precipitated as colourless crystals (0·1 g) from the oxime (0·2 g) in chloroform (10 cc) by passage of dry hydrogen chloride for 5 minutes and leaving for 30 minutes at 0°.

Acetothiophthienoxime hydrochloride (L) was also obtained from the oxime (0·5 g) in chloroform (10 cc) by addition of acetyl chloride (2 cc) at 0° and leaving for 2 hours at 0°. Pale yellow crystals (0·3 g) separated, m.p. 163° (decomp) and 169° to 172° (decomp) on slow and rapid heating respectively. The aqueous solution contained hydrochloric acid. (Found : Cl, 14·4; $C_8H_8ONClS_2$ requires Cl, 15·2 per cent.)

The two products were identical as shown by m.p. and mixed m.p. (slow heating), and that obtained using hydrogen chloride did not depress the m.p. of the insoluble precipitate formed from thionyl chloride and the oxime in acetone at 0°, see p. 397. The hydrochloride is immediately decomposed by water or alcohol, re-forming the oxime, m.p. 160°. It is insoluble in chloroform, acetone, or ethyl acetate.

Reduction of Nitrothiopththen (L) to Acetylaminothiopththen (LN)

Nitrothiophthen (L) was prepared from liquid thiophthen by a modification of Challenger and Harrison's method.[5] Quantities : liquid thiophthen 3 g, acetic anhydride 2 cc, acetyl nitrate (1 cc nitric acid (*d* 1·52); 10 cc acetic anhydride). Addition of the acetyl nitrate requires 25 minutes at −10°. Unchanged liquid thiophthen was removed by washing the product of steam-distillation with a little light petroleum. Yield of nitrothiophthen (L) 1·1 g; 30 per cent, m.p. 125·5°. A black solid removed after steam distillation. This has not yet been examined. Two repetitions of this preparation gave the same yield.

Reduction. Nitro-L thiophthen (1·0 g) in acetic anhydride (10 cc) was reduced by hydrogen and Raney nickel (0·3 g) at N.T.P. The catalyst soon became poisoned. It was removed, and 1·0 g fresh catalyst added. No further difficulty was encountered. Adsorption time 2 to 2½ hours. The catalyst was then removed, and the mixture poured into sodium bicarbonate solution. The crude acetylated amine (0·9 g, 85 per cent yield) of m.p. 218°, was crystallized to constant m.p. 221·5° from ethyl alcohol, charcoal being added. The m.p. was unchanged on recrystallization from ethyl or methyl alcohol or on admixture with acetylaminothiophthen (LK), m.p. 221·5°, see p. 400. This substance was also identical (m.p. and mixed m.p.) with the acetylated amine (LN) of Challenger and Harrison [5] prepared by reduction of the nitro-compound with stannous chloride, followed by acetylation.

At 223° slight decomposition and darkening occur. (Found : C, 48·6; H, 3·8; N, 7·06. $C_8H_7ONS_2$ requires C, 48·7; H, 3·5; N, 7·1 per cent.)

Derivatives of Solid Thiophthen

Conversion of Iodothiophthen (S) to Thiophthenoic Acid (SI) through the Grignard Reagent

Iodothiophthen (S), m.p. 49°, was prepared from solid thiophthen by the procedure described for the liquid isomer (see p. 399), and crystallized to constant m.p. from light petroleum. Yield 20 per cent. This substance decomposed within two to three days, and no attempt was made at analysis. It was converted to thiophthenoic acid (SI), through the Grignard reagent by treatment with carbon dioxide as described for the liquid isomer, see p. 399. The acid was crystallized to constant m.p. 223° from chloroform and from water. Yield : 20 per cent. The methyl ester (SI) prepared by means of diazomethane had m.p. 98°. In admixture with (SK) thiophthenoic acid of m.p. 223° (prepared by oxidation of the methyl ketone by the method of Challenger and Gibson,[2] who give m.p. 220° to 220·5°) the m.p. of the acid (SI) was also 223°. Similarly, the methyl esters (SK) (Challenger and Gibson [2] give m.p. 97°) and (SI) were identical. (Found for the thiophthencarboxylic acid (SI) : C, 45·7; H, 2·3. $C_7H_4O_2S_2$ requires C, 45·7; H, 2·2 per cent.)

Preparation of Acetylaminothiophthen (SK) by the Beckmann transformation of acetothiophthienoxime (S)

The acetothiophthienone (S) was usually prepared from solid thiophthen, acetyl chloride, and stannic chloride in carbon bisulphide by the method

used by Challenger, Clapham, and Emmott [1] for the corresponding ketone of liquid thiophthen. It can, however, be obtained by the use of iodine in place of stannic chloride. A mixture of solid thiophthen (1·7 g), acetic anhydride (1·5 cc), and iodine (0·013 g), on heating at 110° for 45 minutes, gave 1·0 g of crude acetothiophthienone (S), m.p. 121° in 50 per cent yield.

This Beckmann change was carried out as described for acetothiophthienoxime (L) (see p. 400). The ketoxime (S), m.p. 168°, was prepared from acetothiophthienone (S) by the method of Challenger and Harrison,[5] who give m.p. 172° to 173°. On transformation of 1 g in acetone (10 cc) with thionyl chloride (0·8 cc) the oxime gave acetylaminothiophthen (SK), m.p. 220° (decomp). Yield 0·85 g; 85 per cent. The product was crystallized to constant m. p. 223·5° (decomp) from ethyl and then methyl alcohol, with addition of charcoal. (Found: C, 48·7; H, 3·8; N, 7·18. $C_8H_7ONS_2$ requires C, 48·7; H, 3·5; N, 7·1 per cent.) The presence of an acetyl group was shown by hydrolysis with sodium hydroxide, extraction with ether, and evaporation of the alkaline solution. Warming the residue with sulphuric acid and alcohol gave an unmistakable odour of ethyl acetate.

Acetothiophthienoxime (S) Acetate and Hydrochloride

The acetate was prepared by the method described for the corresponding derivative of liquid thiophthen, see p. 400. Acetyl chloride (6 cc) was added to the oxime (1 g). Hydrogen chloride was at once evolved and a colourless precipitate formed (presumably the oxime hydrochloride). The mixture was then gently boiled under reflux for 20 minutes. The resulting clear light-brown solution was evaporated to 3 cc and cooled to 0° when the impure oxime acetate (0·5 g, m.p. 117°; 45 per cent yield) separated. Crystallization from ethyl acetate gave the pure compound (0·2 g) in colourless plates, m.p. 120°. (Found: C, 50·0; H, 4·1; N, 5·9. $C_{10}H_9O_2NS_2$ requires C, 50·2; H, 3·8; N, 6·0 per cent.)

Acetothiophthienoxime acetate (S) dissolves slowly in warm dilute sodium hydroxide; on cooling, the sodium salt of the oxime is precipitated. Careful acidification then gives the oxime, m.p., and mixed m.p. 169° in admixture with an authentic specimen, m.p. 172°. On warming the acidified solution the ketone was obtained, m.p. 120° and mixed m.p. 123° to 125° with an authentic sample of acetothiophthienone (S), m.p. 125°.

The hydrochloride, m.p. 175° (decomp), was precipitated from a solution of the oxime in chloroform by dry hydrogen chloride. It can be rapidly recrystallized from alcohol, but with much loss.

It was also obtained from the oxime (1 g) in acetic anhydride (2 cc) and glacial acetic acid (10 cc) with hydrogen chloride gas at 0°. The greenish precipitate (0·3 g), m.p. 145° to 156°, which separated overnight yielded after five crystallizations from alcohol only 0·08 g of the pure hydrochloride, m.p. and mixed m.p. with the product obtained in chloroform solution, 175° (decomp).

Reduction of Nitrothiophthen (S) to Acetylaminothiophthen (SN)

Nitrothiophthen (S), m.p. 125°, was obtained from solid thiophthen and acetyl nitrate by the procedure employed for nitrothiophthen (L) (see p. 401). Yield: 60 per cent.

Reduction. The reductive acetylation using Raney nickel was carried

out as described for nitrothiophthen (L), see p. 401. It was necessary to add a further quantity of catalyst. The impure acetylated amine (SN), m.p. 219° (decomp), when crystallized from ethyl alcohol, with addition of a little charcoal, had m.p. and mixed m.p. 223·5° (decomp), with acetylaminothiophthen (SK) of the same m.p. (Found : C, 48·7; H, 3·8; N, 7·2. $C_8H_7ONS_2$ requires C, 48·7; H, 3·5; N, 7·1 per cent.)

Further Experiments on the Reduction of Nitrothiophthen (S)

Attempts to reduce the nitro-compound with stannous chloride, tin, zinc, or iron in aqueous or alcoholic hydrogen chloride solution gave a brown infusible product, seemingly a polymer. Compare the effect of strong acids and tin or iron on derivatives of thiophen (Challenger, Miller, and Gibson [11]). Ferrous hydroxide had no action on a warm aqueous alcoholic solution of the nitro-compound. Ammonium hydrogen sulphide appeared to give traces of the amine, but much polymerization occurred.

Slightly better results were obtained by reductive acetylation. Zinc dust (5 g) was added in one portion to a well-shaken solution of nitrothiophthen (S) (1 g) in a mixture of acetic anhydride (7 cc) and acetic acid (7 cc) at 30°. Water (3 cc) was then added. Reaction and rise of temperature occurred at once. After warming at 100° for 5 minutes, the excess of zinc was separated and the filtrate partly neutralized with aqueous sodium bicarbonate. A brown solid (0·5 g) separated and was dried and boiled with alcohol and charcoal and filtered. The filtrate gave a colourless solid, unmelted below 250°, in amount insufficient for analysis. Concentration of the alcoholic mother liquor gave about 5 mg of crude acetylaminothiophthen (SN) as slightly brown crystals, m.p. 220° (decomp) and mixed m.p. 222°, with acetylaminothiophthen (SK), m.p. 223·5°, see p. 402.

The Structure of Liquid Thiophthen

Nitration of the Methyl Ketone to Nitro-acetothiophthienone (LKN)

Nitric acid (0·25 cc) was added drop by drop with vigorous shaking to a solution of acetothiophthienone (L) (0·7 g) in acetic anhydride (10 cc) initially at 40°, during 2 to 3 minutes. The temperature rose to 50°. The nitro-ketone, m.p. 219°, crystallized from solution. After standing at 0° for 1 hour, the product was collected. A further small amount was precipitated from the mother liquor on pouring into sodium carbonate solution. Yield : 0·55 g; 65 per cent. In addition, 0·1 g of a dark-brown product of m.p. 140°, insoluble in sodium carbonate, was obtained. This was very soluble in acetic anhydride, and could therefore have contained only traces of the nitro-ketone which is sparingly soluble in this solvent.

The nitroacetothiophthienone (LKN) was crystallized to constant m.p. 220° from ethyl alcohol and then acetic acid, a little charcoal being added. (Found : C, 41·7; H, 2·2; N, 5·88. $C_8H_5O_3NS_2$ requires C, 42·2; H, 2·2; N, 6·0 per cent.)

The nitro-ketone is very slightly soluble in sodium carbonate or acetate solutions, giving a deep red colour.

The oxime was prepared from the nitro-ketone (2·8 g), barium carbonate (3·4 g), hydroxylamine hydrochloride (2·2 g), and ethyl alcohol (50 cc) by refluxing for 12 hours. The barium salts were removed and washed with

hot alcohol. On evaporation the combined liquors gave the crude oxime (2·8 g), m.p. 229° (decomp), as yellow crystals which were easily soluble in warm dilute aqueous sodium hydroxide forming a red sodium salt, whereas the original nitro-ketone was insoluble. Nitro-acetothiophthienoxime (LK) on two crystallizations from ethyl alcohol had m.p. 230·5° (decomp). (Found : C, 40·2; H, 2·7; N, 11·7. $C_8H_6O_3N_2S_2$ requires C, 39·7; H, 2·48; N, 11·5 per cent.)

Conversion of the Nitro-Ketoxime to Nitroacetylaminothiophthen (LK) by the Beckmann Transformation

Thionyl chloride (0·4 cc) was added during 20 seconds with shaking, to a solution of nitro-acetothiophthienoxime (LK) (0·2 g) in acetone (5 cc). The nitro-acetylamine which separated was recrystallized from alcohol, forming orange prisms, m.p. 259° (decomp). Yield : 0·15 g; 75 per cent. The m.p. was unchanged on crystallization from ethyl alcohol. (Found : C, 39·0; H, 2·6; N, 11·5. $C_8H_6O_3N_2S_2$ requires C, 39·7; H, 2·48; N, 11·5 per cent.)

Preparation of Nitro-acetothiophthienone (LNK) from Nitro-thiophthen (L)

A solution of nitrothiophthen (L) (1·0 g) and acetyl chloride (1 cc) in carbon disulphide (20 cc) was added to anhydrous aluminium chloride (3 g) suspended in carbon disulphide (5 cc) and the mixture left overnight. Hydrogen chloride was slowly evolved during the first 2 hours. The addition compound was decomposed by ice and hydrochloride acid; the nitro-ketone (0·6 g; 60 per cent), m.p. 180° to 200°, was precipitated. The carbon disulphide layer gave 0·2 g of unchanged nitrothiophthen (L). The nitro-acetothiophthienone (LNK) was crystallized to constant m.p. 220° from ethyl alcohol and then acetic acid, with addition of decolorizing charcoal, see p. 403. In admixture with the nitro-ketone (LKN) of m.p. 220° (see p. 403), the m.p. was also 220°. No other nitrated ketone and practically no polymer was detected. An attempt to carry out the Friedel–Crafts reaction using stannic chloride as catalyst, failed. The nitro-thiophthen was recovered unchanged. (Found : C, 42·2; H, 2·4; N, 6·4. $C_6H_5O_3NS_2$ requires C, 42·2; H, 2·2; N, 6·2 per cent.)

The Oxime, nitro-acetothiophthienoxime (LN) had m.p. and mixed m.p. 230·5° (decomp) with the (LK) nitro-ketoxime of m.p. 230·5° (decomp), see above. The preparation and purification of the two specimens were identical. (Found : C, 40·1; H, 2·9; N, 11·6. $C_8H_6O_3N_2S_2$ requires C, 39·7; H, 2·48; N, 11·5 per cent.)

Nitration of Thiophthenoic Acid (LK)

(LK) Thiophthenoic acid (LK) was obtained by oxidation of the methyl ketone with sodium hypoiodite by a modification of Challenger and Gibson's [2] method. Quantities : ketone, 7·3 g; 5*N*-NaOH, 50 cc; pyridine, 40 cc; iodine solution (iodine 31 g), potassium iodide (60 g), in water (300 cc). Time of addition 4 hours; left overnight. Yield of crude carboxylic acid, m.p. 240° (decomp), 5·5 g; 75 per cent. The pyridine increases the solubility of the ketone in the reaction mixture.

Nitration. Nitric acid (0·4 cc; *d* 1·52) was added drop by drop with shaking during 10 to 20 seconds to a solution of crude thiophthenoic acid

(1·0 g) in acetic anhydride (10 cc) initially at 40° to 50°. The nitro-acid rapidly crystallized from solution. The mixture was left overnight at 0°. The acid was purified from traces of its anhydride by dissolving in sodium hydroxide, filtering, re-acidifying, and extracting with ether, yielding impure (LK) nitrothiophthenoic acid, m.p. *ca* 285° (decomp.) (0·6 g; 60 per cent). Two crystallizations from acetic acid, with addition of a little charcoal, gave the nitro-acid in pale yellow needles. The rather indefinite m.p. was 285° (decomp). (Found: C, 37·1; H, 2·2; N, 6·5. $C_7H_3O_4NS_2$ requires C, 36·7; H, 1·3; N, 6·1 per cent.)

The *methyl ester* was obtained with ethereal diazomethane, and crystallised as very pale yellow needles of constant m.p. 164° from methyl alcohol. (Found: N, 5·5. $C_8H_5O_4NS_2$ requires N, 5·75 per cent.)

Decarboxylation of Nitrothiophthenoic acid (LK) to Nitrothiophthen (LK)

Copper powder (0·1 g) was added to nitrothiophthenoic acid (LK) (0·4 g) in quinoline (3 cc), and the mixture refluxed for 20 minutes. Addition of excess hydrochloric acid, and distillation in steam, gave nitrothiophthen (LK) (0·1 g; 30 per cent) of m.p. 124° to 125° and 125° on crystallization from ethyl alcohol. In admixture with nitrothiophthen of m.p. 125·5° (obtained by direct nitration of liquid thiophthen) the m.p. was 125°.

An attempt to carry out the decarboxylation by heating with soda-lime followed by distillation in steam was unsuccessful.

ACKNOWLEDGMENTS

The authors thank Imperial Chemical Industries Ltd. for a grant which has defrayed some of the expenses of this research and the Minister of Education for a maintenance award to R.E.

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OBITUARY

RICHARD PATON BROWNLEE

R. P. BROWNLEE, of the National Oil Refineries Limited, Llandarcy, whose sudden death occurred on May 9, 1951, in his sixty-sixth year, was born in Edinburgh in September 1885, and was educated at Stewarts College, Edinburgh (1892–1904), and subsequently served his apprenticeship with a Public Analyst. Prior to joining the Staff of the National Oil Refineries he was employed by various chemical and engineering concerns in Birmingham and the Midlands area. He joined the Staff of the National Oil Refineries as Works Chemist in January 1922, and subsequently served in various capacities on the production management side of the refinery operations; at the time of his death, he was Technical Advisor to the Management, with the specific responsibility for safety matters and implication of regulations covered by various Government Orders and Factory Acts. He served on the Safety Sub-Committee of the Engineering Committee of the Institute of Petroleum, and was a Fellow of the Institute of Petroleum. He was a Member of the Institute of Petroleum, South Wales Branch, from its earliest days, and was, for a time, a Member of the Branch Committee.

In his younger days, he was an enthusiastic fisherman and a useful shot with both small-bore and Service rifles. He was an expert amateur gardener, and was in demand as a judge at local Horticultural Shows.

Despite his thinly veiled brusquesness, he was a lovable character with a gift of human understanding and sympathy, which made him a " Guide, philosopher, and friend " to his colleagues and employees of the National Oil Refineries, many of whom will recall with gratitude his able help and advice in their younger days.

His passing will be regretted by his many friends in various parts of the world. He is survived by a widow, a daughter, and a son.

E. J. H.

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Oilfield Exploration and Exploitation

Geology

1572. Clay mineralogy and the petroleum industry. R. E. Grim. *World Oil*, Mar. 1951, **132** (4), 61.—Relationships between clay mineralogy and the discovery and recovery of oil are described. International co-operation in the field of clay mineral research is emphasized.

Recent work has shown that there are general correlations between the composition of clay minerals and the environment of deposition; illite and chloritic minerals are prevalent in lagoonal sediments, and kaolinite in non-marine sediments. Clay minerals may also have behaved as catalysts in the transformation of organic material to petroleum, and careful research, particularly on the montmorillonites, might provide evidence of this activity.

Eleven references are included. C. A. F.

1573. Sedimentary basins and oil occurrence. L. G. Weeks. *World Oil*, Mar. 1951, **132** (4), 71.—The general relationships between the history of sedimentary basins and the distribution of oil pools contained within them are described. Depositional basins or geosynclines can be related to either the mobile belts or the stable regions. In the mobile belts the long geosynclines consist of a series of *en echelon* troughs separated by saddles. In the stable regions the basins are generally synclinal sags or of graben type.

The incidence of oil occurrence is high in the mobile belts, and it is estimated that 80% of the recoverable hydrocarbons in the world are accumulated in belts comprising only 20% of the total sedimentary basin area. C. A. F.

1574. Northwest Arkansas test. P. C. Ingalls. *Oil Gas J.*, 28.12.50, **49** (34), 105.—No commercial production has been found in northwestern Arkansas, but a well which is being drilled near the southern edge of the Ozark Dome in Johnson County has found several dry gas shows below 1400 ft.

Gas has been produced in the Arkansas Valley from Pennsylvanian–Atoka since 1902. 1 Barton, Johnson County, was recently completed as a gas producer from the Pennsylvanian Morrow. C. A. F.

1575. Maryland gas discovery spurs Deer Park structure activity. Anon. *Oil Gas J.*, 16.11.50, **49** (28), 195.—1 N. K. Welch, Garrett County, Maryland, has found gas on the Deer Park anticline at 2835 ft in Huntersville chert. Final test production was 8,029,000 cu.ft/day. This is the first major gas discovery in Maryland. C. A. F.

1576. Rocky Mountain wildcat ventures. Anon. *Oil Gas J.*, 14.12.50, **49** (32), 63.—1 Meridian Unit, White Pine County, Nevada, the deepest well in the state, was completed as dry at 10,314 ft. Small amounts of paraffinic oil had previously been reported in the area.

Four dry wells have been completed in Idaho. C. A. F.

1577. Wildcats attack Beckham area puzzle. P. C. Ingalls. *Oil Gas J.*, 14.12.50, **49** (32), 137.—There is evidence of compression faulting along the front of the Wichita

Mountains in Oklahoma, and this may control traps in the granite wash. The Elk City field in the Anadarko basin may be an arch which is older than the Wichita Amarillo Uplift.

A number of wildcats have been drilled recently in Beckham County. 1 State-Taylor on a test at about 300 ft flowed gas at 75,0000 cu. ft/day and recovered 2000 ft of 41·7° oil. Pay is Pennsylvanian granite wash. C. A. F.

1578. Bold step out opens new area at Hull. P. C. Ingalls. *Oil Gas J.*, 9.11.50, **49** (27), 201.—Production has been found down dip from the Eocene–Yegua producing area on the western rim of the Hull salt dome, Liberty County, Texas. The two producing areas may be separated by a fault or stratigraphical break. The discovery well, 1 E. F. Failor, on completion flowed 330 b.d. of 40° oil from the Yegua at 7678 to 7690 ft.

Cumulative production of the Hull field, which was discovered in 1918, is over 100 million brl, from zones ranging from 1000 to 7000 ft in depth.

A field has been discovered north of the salt dome, where the accumulation is in a separate reservoir controlled by faults. C. A. F.

1579. New Ellenburger area excites Texans. P. C. Ingalls. *Oil Gas J.*, 2.11.50, **49** (26), 117.—1 Blanche Young in Kent County, which was completed for 1475 b.d. of 41° oil from the Ellenburger, is the first major producer on the Eastern Platform of the Permian basin. It is sited on a structure which is probably a local feature on a regional northwesterly trending nose. Similar structures may exist along the eastern flank of this nose. C. A. F.

1580. Devonian stratigraphy of Rocky Mountains and foothills between Crowsnest Pass and Athabaska River, Alberta, Canada. F. G. Fox. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (4), 822–43.—Devonian rocks were first recognized in the Rocky Mountains in 1886, in the Banff area. Since that time they have been examined, subdivided, and named by a number of workers.

This paper is based on a study of twenty-four Devonian sections, most of which are located between the Bow and Athabaska river valleys.

In the Athabaska Valley the Devonian is divisible into four formations, which are in ascending order: the Flume dolomite, Perdrix shale, Cheviot limestone and dolomite, and Palliser dolomite. On the southeast, near the North Saskatchewan River, the Perdrix shale disappears, due to a rather abrupt facies change, and from this point to Banff and beyond, two formations embrace all of the Devonian rocks. These are the Fairholme and Palliser formations. The Palliser formation extends from Crowsnest Pass to the Athabaska River without significant change in lithologic character or thickness. Most of the beds are Upper Devonian in age, but the Flume may be very late Middle Devonian.

Although good progress is being made in achieving understanding of the Devonian sequence, much additional work remains to be done in the Alberta Rockies.

E. N. T.

1581. Geology of Turner Valley oil and gas field, Alberta, Canada. W. B. Gallup. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (4), 797–821.—The Turner Valley oil and gas field is approx 25 miles southwest of the city of Calgary on the outer or east edge of the foothills of the Rocky Mountains. The first well was drilled on Sheep River in 1913 and completed as a gas well in the Lower Cretaceous. The discovery well in the Paleozoic, Royalite No. 4, blew in in 1924, producing 500 b.d. of naphtha.

The Turner Valley structure is a typical example of an eroded anticline, particularly north of the Sheep River. The softer core of marine Alberta shales has been exposed and eroded to form the floor of the topographic feature known as Turner Valley. East- and west-dipping sandstones of the Belly River formation provide the respective rim rocks of the valley which disappear northward downplunge.

Structurally, the Turner Valley field is comprised of two Laramide structures, the Turner Valley and Millarville thrust sheets, the latter over-riding the down-plunging north extension of the former. The ancestral fold and age of accumulation are pre-Jurassic and pre-Blairmore. The reservoir rock is a dolomitic biostrome identified by the abundance of detrital crinoids etc., which form the porous zones and provide source.

This relationship between the early accumulation and the age of folding, together with the organic origin of the reservoir, is significant in prospecting for oil in the Paleozoic rocks of the Foot-hills and Western Plains areas. E. N. T.

1582. Structural interpretation of loci of petroliferous parts of Devonian reefs in Edmonton area, Alberta, Canada. R. L. Rutherford. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (4), 822–43.—The newly discovered oilfields of the Edmonton district have attracted much attention for the reason that they have been found so close to transportation and in areas of easy access to exploration and development.

This paper is a discussion of the salient features of the structural position of these oilfields in respect to the mountains and foot-hills front on the west and pre-Cambrian terrain on the east.

With the discovery of the Leduc field early in 1947, impetus was given to extensive exploration on the plains. The first reaction was to try to extend the programme southward into the deeper parts of the basin and in the general direction of Calgary. Before this programme had progressed very far, Redwater was discovered in September 1948, and the areas northeast became attractive and competitive with those at the south. Some measure of success was attained in a southern direction by the discovery of the Stettler field, but to date very little drilling has been done on the vast areas taken under reservation south of Red Deer. No tests have been drilled in this southern region in what appears to Rutherford to be the most promising areas on the basis of regional surface geology. E. N. T.

1583. St Mary River formation in Spring Coulee–Magrath area, Alberta, Canada. E. P. Williams. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (4), 885–98.—The St Mary River formation of Upper Cretaceous age is well-exposed along the banks of the river for which it is named, in the vicinity of Magrath and Spring Coulee in southwestern Alberta. The interbedded sandstones and shales of this formation crop out for a distance of more than 25 miles along the deeply incised winding course of the river.

The broad aspects of the stratigraphy of the Upper Cretaceous St Mary River formation, and certain pertinent details are presented of both structure and stratigraphy of the well-exposed section along the St Mary River in southwestern Alberta. The formation thickness is approx 1160 ft; a thick upper member and a thin basal member are differentiated. E. N. T.

1584. Stettler oil field, Alberta, Canada. R. P. Lockwood and O. A. Erdman. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (4), 865–84.—The Stettler oilfield, producing from the $D2^4$ and $D3^4$ zones of the Upper Devonian, was discovered in May 1949. The field is in the central plains area of the Province of Alberta.

The Stettler area is in the extensive Western Canada sedimentary basin, which stretches north from Montana to the Arctic Ocean, a distance of about 1600 miles, and eastward from the Rocky Mountains to the Canadian Shield (pre-Cambrian Shield) in Manitoba, about 800 miles. The Stettler field lies on the eastern edge of the Alberta syncline, one of the major features of the large sedimentary basin. The formations dip gently westward from Stettler towards the Foot-hills, whereas eastward the beds rise gradually towards the Canadian Shield.

The field was found by detailed seismographic and structural core drilling. The producing reservoir was found in two reefoid zones of Upper Devonian age. As at December 15, 1950, there were twenty-three producing wells in the field, eight of which are producing from the D3 zone. The field has not been delineated to date, but extends 4 miles north–south, and 1½ miles east–west. Lower Cretaceous gas and oil have been found 5 miles west of the Devonian field, and a second pool is located 3½ miles northeast. Only beds of Cretaceous, Mississippian, and Devonian age have been drilled in the field. E. N. T.

1585. Source of oil in "tar sands" of Athabaska River, Alberta, Canada. T. A. Link. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (4), 854–64.—The increasing recent interest in the possibilities of extracting oil from the "tar sands" of Athabaska make this paper particularly timely.

The geologic cross-section through central Alberta indicates an unconformity of considerable magnitude at the base of the Lower Cretaceous sediments, and it also depicts

progressively deeper bevelling of Lower Mesozoic and Upper Paleozoic sediments from west to east, so that in the Alberta syncline, along the Foot-hills Front, the Lower Cretaceous beds rest on Jurassic rocks, thence eastward on Mississippian, Devonian, Silurian, and finally pre-Cambrian beds.

The " tar sands " of the Athabaska or " McMurray bituminous sands " of Lower Cretaceous age in northeastern Alberta, Canada, are believed to have derived their bituminous content from the underlying coral-reef reservoirs of Upper Devonian age which come in contact and near-contact with the overlying sands at the unconformity between the Lower Cretaceous and the Devonian. The white quartz sands were supplied from the pre-Cambrian " Athabaska sandstone " lying at the northeast on the Canadian Shield, and it is suggested that the escape of oil and gas through fissures and fractures from the Devonian reservoirs into the " tar sands " occurred primarily during, but also possibly subsequent to, the deposition of the Cretaceous " tar sands." It is also believed that the Lower Cretaceous heavy oil of Lloydminster, Alberta, has had a similar history. E. N. T.

1586. Tectonics of east side of Cordillera in Western Canada. A. J. Goodman. *Bull. Amer. Ass. Petrol. Geol.*, 1951, **35** (4), 783–96.—In western Canada the epicontinental Devonian seas once covered the site of the present Rocky Mountains as far west as the Rocky Mountain trench, extending eastward at least as far as the present edge of the pre-Cambrian Shield in Saskatchewan and Manitoba. It appears doubtful if true geosynclinal conditions ever existed in the western part of this area at this time, although the thicker deposits indicate deeper waters there.

In defining the limits of the western Canadian oil province of Paleozoic age, the eastern side of the Cordillera must be included as potential oil territory wherever structural and erosional conditions appear favourable. This conclusion is supported by oil and gas occurrences at Pincher Creek, Turner Valley, Jumping Pound, Norman Wells, and in minor amounts at many other places in the foot-hills.

The mechanics of formation of these mountain ranges is in consequence of practical importance, not only for the understanding of structural effects in both the mountains and foot-hills, but also for a more complete understanding of the foreland or Plains area.

The main Rocky Mountains and their foot-hills have been strongly compressed and have developed overthrusts directed towards the east. The beds of the foreland or Plains area are comparatively flat and undisturbed.

The main Mackenzie Mountains are open folds with some normal faulting. Their foreland has been broken by block faulting of the basement, through which most of the mountain-building stresses were transmitted.

By applying information obtained from the Mackenzie Mountains foreland to problems of the Rockies it becomes apparent that in the geosynclinal belt the basement was so deep and so broken that it was ineffective to control structure. The Paleozoic limestones were the agents of structural control in this tectonic belt.

In the Plains the basement was rigid and unyielding except in a few localities.

The degree of yielding to compression is a measure of relative strength of the basement and of the other rocks in the sequence in different localities, and bears little relation to the intensity of compressive stress present in a particular locality. With this understanding of basement control more logical interpretations of characteristic structures of the Rocky Mountains and foot-hills can be given.

Chamberlin's concept of basement control coupled with the evidence from the Mackenzie foreland point to the conclusion that stress effects on the eastern side of the Cordillera are not necessarily a measure of local stress; but they are a measure of the varying strength of the strongest member of the rock sequence at any point. The idea that stress was present only where its effects can be observed has led to the erroneous idea that the Rockies were built by a push from the west with a dying-out of this force on the western edge of the Plains area. E. N. T.

1587. Chilean discovery. Oil production found in Cerro Sombrero region. Anon. *Oil Gas J.*, 30.11.50, **49** (30), 55.—A second well drilled in one of several structures in the Cerro Sombrero area, Chile, was completed for approx 300 b.d. of oil similar in quality to the Cerro Manantiales crude.

Plans are to lay a line from the new field to that connecting Cerro Manantiales with the terminal at Caleta Clarencia. C. A. F.

1588. Lacq. A new French oilfield. Anon. *Petroleum*, Mar. 1951, **14** (3), 69.—Exploration in France since the war has centred in the southern part of the country between the Mediterranean and the Atlantic coasts. Gas has been found near Saint-Marcet in the Pyrennean foot-hills, and this is now being piped to Bordeaux and elsewhere.

As a result of reflection surveying on a dome in 1950, an oilfield was discovered at Lazq near Pau in the foot-hills of the Pyrenees. The discovery well found pay at 2040 ft and initially flowed oil at a max rate of 7700 b.d. from Lower Senonian dolomitic limestone. Five wells have been drilled in the field, and the oil, which is of good quality, is being railed to the refinery at Pauillac.

The oil accumulation may be related to the Puyoo fault, which trends approx northwest–southeast to the south of the field, and the structure may be diapiric, as are many of the salt structures in southwestern France. C. A. F.

1589. Oil and gas in Italy. Anon. *Petrol. Engr*, Feb. 1951, **23** (2), A–50.—Several structures in Italy have been drilled as a result of recent seismic work; of sixty wells drilled since the war, two are producing oil, and the remainder, excepting four to five dry holes, are producing gas.

The structures are in the Po Valley, and four have been tested. These are the Caviaga, Cortemaggiore, Ripalta, and Soresina anticlines.

Nineteen wells have been drilled in the Caviaga field, which produces gas from the Miocene Messinian sands. Total daily production is approx 34 million cu. ft.

The Cortemaggiore field, 25 miles southeast of Caviaga, also produces gas from the Messinian. Pay is at about 5000 ft and eighteen wells have been drilled with a potential production of approx 60 million cu. ft.

The Ripalta field, 6 miles north of Caviaga, found gas in the same zone, and five wells have been drilled, with a total production of 20 million cu. ft.

The Soresina field, 8 miles southeast of Ripalta, found gas in the Miocene Tortonian sand and other zones.

Structures are also being drilled at Pontemure and Cornegliano, both anticlinal. Shallow holes have also been drilled in the Polesine area near the mouth of the Po River.

A pipeline network is under construction. A 3-inch line from Cortemaggiore to Milano will have a capacity of approx 70 million cu. ft. C. A. F.

Geophysics and Geochemical Prospecting

1590. Sand bar located by seismograph. P. C. Ingalls. *Oil Gas J.*, 26.10.50, **49** (25), 141.—Seismic waves travel at a slower rate through fluid-saturated rocks than in dry rocks, and it is possible to locate saturated sand lenses by measuring time differences between two essentially parallel reflecting horizons. These "time thicknesses" will show the presence of a relatively slow velocity formation which may be oil-bearing.

Experiments along these lines have been carried out at the South Ceres pool in Oklahoma with considerable success in an extension area north of the field.

C. A. F.

1591. Weathering and other surface shooting problems. N. Clayton. *World Oil*, Mar. 1951, **132** (4), 57.—Weathering problems in the use of the Poulter or surface shooting method in seismic exploration are described. The Poulter method has its max utility in areas where the record quality of surface shots is superior to those obtained from shot holes. C. A. F.

Drilling

1592. Know your drill collar. T. B. Morris. *World Oil*, Dec. 1950, **131** (7), 106.—The increased depth of production zones and of exploratory wells emphasizes numerous problems; many of the drill-collar failures are attributed as much to mechanical handling as to defective steel. Metallurgical factors contributing to failure are discussed fully. A. J. H.

1593. Research reveals fatigue results for pipe-to-tool joints. Anon. *World Petrol.*, 1951, **22** (3), 58–60.—Machine is described for field and laboratory examination of failures at drilling-tool/pipe joints and for investigating relative strengths thereof. Failure usually occurs in pipe-to-tool joint subject to bending, torsion, tension, and compression. Machine consists of a rotating spindle (300 r.p.m.) for holding a 10-ft pipe section with tool joint installed. Weight is mounted on roller bearing at end of pipe to apply bending load. Several classes of joint were examined; fatigue failure stress determined after 1,000,000 cycles ranged from 15,000 p.s.i. (regular API threaded connexions) to 23,000 p.s.i. (flash-welded joints). E. B.

1594. Well blow-outs in California drilling. Part I. A. J. Horn. *World Oil*, 1950, **131** (5), 99. **Part II; 131** (6), 132.—The cases of a number of blow-outs in California are reviewed; in this paper only the blow-outs which actually resulted in injury to personnel, loss of hole, or other serious damage are considered. Fifty-five cases were taken for the study of the causes, and the latter are treated separately.

Formation pressure control is effected primarily by static fluid head, and secondarily by specially installed blow-out-prevention equipment. Original formation pressures of production zones in the California area are approximately equal to a static head of salt water; two cases are quoted as having pressure gradients equivalent to geostatic load.

Factors contributing to blow-outs are: (*a*) Reduction in fluid level by lost circulation; this is dangerous owing to its unpredictable, and often rapid, occurrence. Induced lost circulation may be the result of running-in pressure, excessive fluid density, or type of fluid. (*b*) Insufficient fluid density, encountered in unknown drilling areas, or induced by gas-cutting. Only means of countering this fault is by increasing mud density well in excess of safe limit; conditioning of the mud at the surface is essential. (*c*) Reduction in pressure by pipe withdrawal was the cause of 16% of the reported blow-outs. Large pressure reductions encountered on withdrawal of pipe after cementing operations were particularly significant, and are due to the build-up of mud-gel strength. (*d*) Failure to keep the hole full contributed to 42% of blow-outs.

In Part II preventive measures are described. (*a*) Knowledge of surrounding wells and possible zones of lost circulation reduce the possibility of rapid loss of mud. The availability of remedial materials, high-visc mud, and cementing off the loss zones are included in the necessary planning arrangements. The installation of a pit-level indicator, although not of widespread application, would serve to warn the driller of mud loss; frequently, the loss is initially gradual. (*b*) When operating in fields of complex fault structures at depths below 300 ft it is advisable to maintain a mud pressure 500 p.s.i. in excess of the formation pressure. A recording mud-density meter also assists the driller in observing any reduction in density as a result of gas-cutting or water dilution; in the event of gas contamination, steps should be taken to de-gas the mud. (*c*) The maintenance of a low gel strength is important. (*d*) Failure to keep the hole full is itself inexcusable, and should be avoided by the circulation of mud into the annular space; this is particularly important in the event of withdrawing plugged pipe.

Secondary control should be adequate, incorporating a complete shut-off valve, an annular closure device, and a bag-type closure. The installation of good equipment should be followed by its maintenance in efficient working order.

Analysis of blow-outs is given in graphical and tabular forms.

References. A. J. H.

1595. Gulf Coast hurricane design data. A. H. Glenn. *World Oil*, Dec. 1950, **131** (7), 101.—Problems of design are discussed with regard to hurricane forces on structures, and the relatively weak foundations of the Gulf Coast. The progress of the "storm tide" and the factors which contribute to its formation are discussed. The principal difficulty in assessing values is due to the lack of representative data over a period of time.

References. A. J. H.

1596. Thermal stresses around an uncased hole. K. D. Saunders and A. D. Topping. *World Oil*, Dec. 1950, **131** (7), 167; Jan. 1951, **132** (1), 155.—The well is compared to a thick-walled cylinder, the outer dia approaching an extreme. Thermal stresses in

drilling are set up by the formation and circulating fluid. Considering an element, an equation of heat flow is obtained, and its solution proposed by the use of the Laplace transform. The temp gradients after periods of time are determined and plotted.

The variation of thermal stresses with time is nearly linear. Assuming axial symmetry, elastic properties of rocks, and conditions of equilibrium, the stresses occurring in the neighbourhood of the well bore are determined and expressed graphically.

The results are considered in relation to the assumptions made. Sixteen references.

A. J. H.

1597. A new system of electric logging. W. Tapper and W. J. Greer. *World Oil*, Oct. 1950, **131** (5), 119.—Description is given of a frequency modulation (FM) system of electric logging, which, in measuring the formation resistivity, ensures that simultaneous recording of both current and voltage is effected.

Economic considerations necessitate the min of time for logging; thus, either the speed of logging must be increased or more information must be obtained from each run. Several factors limit the former. The FM system has the advantage of recording relevant data without much regard to the characteristics of the suspension cable. The form of the log is discussed with reference to different thickness beds. A. J. H.

1598. Fracture sludge—a basic factor in sand plugging. F. R. Cozzens. *World Oil*, Nov. 1950, **131** (6), 126.—Fracture sludge has been found to contribute to the retarding of repressuring operations. The sludge consists of an oil–water emulsion, infused with gas, and containing shattered elements of the sand structure, and is formed particularly just prior to the well-servicing. Field experience has shown also that about 50% only of the total sludge is removed in well clean-outs.

In the event of insufficient clean-outs of input wells, the remaining sludge is forced back into the well-bore, and conditions develop suitable to organic growth and mineral deposition. Measures must necessarily be preventive, as no effective system has been devised for the complete removal of sludge; principally, excessive shattering of the formation should be avoided. Allowing time for drainage into the well, between successive bailing, assists in cleaning the fractured system.

The nature of various sludges is considered. A. J. H.

1599. Oil emulsion drilling mud. O. van Dyke. *World Oil*, Nov. 1950, **131** (6), 101.—Advantages of oil-emulsion drilling mud include increased drilling rate, longer life of drilling bits, and reduction of rotating friction. An introduction to emulsion is given, the preparation of such emulsions necessitates the mixture of oil and water by the application of work, or by the addition of an emulsifying agent. Emulsifiers consist of non-polar polar type of structure, the non-polar portion of the molecule being soluble in oil, and the polar in water. Finely divided clay may also act as an emulsifier.

Oil-emulsion mud is treated in the same way as water-base muds; the only difference in rig operation is the requirement for oil-resistant rubber connexions. It is convenient to consider oil-emulsion muds as normal drilling muds with certain improved qualities. The optimum concentration has been found to be about 20% by volume. Drilling by emulsion mud has frequently resulted in higher productivity, other factors being equal; this improvement is attributed to the better wall-building properties of the mud, and the low surface tension of filtrate from such muds. Various field results are analysed. A. J. H.

Production

1600. Empirical method of measuring oil pool performance. C. Beal. *World Oil*, Nov. 1950, **131** (6), 168.—An introduction is given to the Y factor, which is the productive behaviour of a pool in terms of the number of barrels produced per 1000 p.s.i. decline per acre foot. A secondary term Y_0 also includes the interstitial water saturation and porosity of the formation.

Values of Y range between 15 and 30, above the bubble point, and between 60 and 70 below the bubble point. The use of this factor lies in the prediction of (1), reservoir performance in the early stages of production before adequate data are accumulated; (2) ultimate oil recovery; (3) original reservoir volume in depletion-type reservoirs; (4) volume of oil movement between wells.

115 oil pools are considered, and it has been shown that definite correlation may be demonstrated between sand reservoirs, and between limestone reservoirs. The limitations of the method are listed, and the conclusions given. Specific cases are considered. References. A. J. H.

1601. Evaluation of zonal damage. N. Johnston and N. van Wingen. *World Oil*, Dec. 1950, **131** (7), 156.—The productivity index, as a measure of the zonal characteristics, is determined primarily by the properties of the reservoir and fluid, and secondarily by the methods of exploitation. The factors affecting sand permeability include: (*a*) The oil saturation varying, in the neighbourhood of the well bore, according to the rate of production. (*b*) Mud-filtrate invasion, which may be temporary if no interaction occurs between filtrate and formation. The use of oil-base mud is advantageous in reducing filtrate invasion. (*c*) Particle invasion, which is dependent on the mud properties.

The equipment and extent of liner perforations are secondary factors. It is recommended that care should be taken to restrict zonal damage to a minimum; although ultimate recovery need not be affected, the rate of production must necessarily be decreased.

References. A. J. H.

1602. Influence of clay in oil production. B. B. Cox. *World Oil*, Dec. 1950, **131** (7), 174.—Clays are not sources of production, but their existence in sands may mislead operators as to the productive capacity of the formation; these misinterpretations may range from supposed absence of a producing zone to a non-productive sand. Previous work had been conducted on an empirical basis, but for a clearer understanding of field problems, laboratory research into the behaviour of clays is necessary. Clays are common, but their particle size has made investigation difficult. The cell structures of kaolinite and montmorillonite are given diagrammatically. The composition and properties of clays are discussed with reference to base exchange. References. A. J. H.

1603. Kansas water floods. K. B. Barnes. *Oil Gas J.*, 4.1.51, **49** (35), 30.—Waterflooding projects were operating in 159 areas in eastern Kansas in 1950, accounting for 28,100 b.d. A total of 4900 oil wells and 4090 injection wells were being used.

The chief zone being flooded is the Bartlesville sand, which is being flooded at 2800 ft in the Fox Bush field in Buttes County. In west-central Kansas the Hunton lime is being flooded at 3300 ft.

Only four fields are being repressured with gas in eastern Kansas. C. A. F.

1604. Tapered sucker rod strings. A. Quayle. *World Oil*, Nov. 1950, **131** (6), 186.—Formulæ are presented for the selection of tapered rod strings. The proportions of various-dia sucker-rod are determined by equating the stresses at the top of each section. On this basis a table has been drawn up, using various plunger dia. The four rod sizes considered are $\frac{5}{8}$, $\frac{3}{4}$, $\frac{7}{8}$, and 1 inch dia. A. J. H.

1605. Permeability surveying and controlled acidizing. B. M. Kingston. *World Oil*, Oct. 1950, **131** (5), 164.—In many cases separate acidizing of formation is not necessary owing to the interconnexion of zones, or to the similar conditions of permeability in adjacent zones. Description of tools and methods (U.S.P. 2,473,713) used for the investigation of the characteristics of separate zones is given with diagrams. The principle consists in tracing by means of an electrode the inter-face of a moving boundary of electrolyte/non-electrolyte. A. J. H.

Oilfield Development

1606. World production resumes upward trend. D. M. Duff. *Oil Gas J.*, 21.12.50, **49** (33), 204.—World production in 1950 averaged 10,377,000 b.d., 11·5% higher than in 1949. In the U.S.A. average daily production was 5,403,000 b.d., or 7·2% more than in 1949.

New production records were established in Venezuela, Canada, Colombia, Mexico,

Germany, the Netherlands, Egypt, British Borneo, and in the principal Middle East areas.

Tables and charts show production in the major world areas, and world production since 1928, by countries. C. A. F.

1607. Completions up 11·5%. Anon. *World Oil*, Mar. 1951, **132** (4), 34.—3766 wells were completed in the U.S.A. in Jan. 1951, at an average depth of 3853 ft.

A table shows well completions in the U.S.A. during Jan. 1951. C. A. F.

1608. Nations' cumulative production nearly 39 billion barrels. Anon. *Oil Gas J.*, 19.11.50, **49** (28), 202.—Approx 39 billion brl have been produced in the U.S.A., since 1859, or two-thirds of the world's cumulative production. 1949 production was 1840 million brl of crude and condensate, 54% of the world's production of 3,407,900 brl.

At the beginning of 1950 there were approx 449,500 producing wells in the U.S.A., of which Texas had 116,000 and Pennsylvania 83,700. In addition, there were 65,000 producing gas wells.

Proved reserves of oil in the U.S.A. are estimated at 24·6 billion brl, and natural gas, 180 trillion cu. ft. C. A. F.

1609. Exploration makes fast start. Anon. *World Oil*, Mar. 1951, **132** (4), 76.—780 exploratory wells were completed in the U.S.A. in Jan. 1951, compared with 782 in the previous month and 636 in Jan. 1950. 19·1% of these wells were successful, and seventy-two oilfields and twenty-three new pays were discovered. Eight distillate and sixteen gas fields were found.

Tables show the results of exploratory drilling in the U.S.A. in Jan. 1951, by states, and the new oil, distillate and gas fields, and new pays discovered in Jan. 1951. C. A. F.

1610. Heavy crudes play heavy role in reversing California's production trend. Anon. *Oil Gas J.*, 9.11.50, **49** (27), A-28.—Crude production in California increased by 55% from 1940 to 1950, and 95% of this output was heavy oil (below 20°). 25,075 wells are producing in the state, and of these 17,750 are producing crudes of less than 25°.

44% of production comes from fields in the San Joaquin Valley, 37% from the Los Angeles basin, and the remainder from fields in the Coastal regions. Cumulative production of the state is over 8·5 billion brl.

The Willington field in the Los Angeles basin, discovered in 1936, has now approx 2000 producers, mostly pumpers, and production is approx 135,000 b.d. Pay consists of seven zones between 2200 and 6000 ft, each several hundred feet in thickness. Cumulative production of the field has reached 500 million brl.

Oil has been discovered in recent years in the Cuyama Valley in the San Joaquin area, where the Russell Ranch field currently produces approx 21,000 b.d. from 134 wells. The Placerita Canyon field, after rapid and unrestricted development, has declined from a peak production of 34,000 b.d. in Sept. 1949 to approx 10,300 b.d. at the present time.

Gas-injection projects have been started in a number of fields in recent years.

Tables show annual crude production and natural-gas withdrawals in California since 1919, the volumes of crude produced by gravities, and new well completions and initial rates since 1941. C. A. F.

1611. Shell activities. D. H. Stormont. *Oil Gas J.*, 30.11.50, **49** (30), 44.—Wells are to be drilled during the next few years to develop proved deep reservoirs in some of California's older fields. These include Ventura, which will have approx 200 additional wells, and Brea. C. A. F.

1612. Moss Bluff revived. J. A. Kornfeld. *Oil Gas J.*, 30.11.50, **49** (30), 45.—Production has been resumed from the Moss Bluff salt dome, Liberty County, Texas, which was abandoned in 1933.

The salt dome is of the piercement type with its major axis trending northwest–southeast. Salt was found at 1160 ft. Commercial production was obtained in 1929 from the Marginulina–Frio at about 5800 ft, but was discontinued within a few years

as production declined. Oil shows are reported in the Middle Oligocene, Discorbis, and Heterostegina zones. A recent well initially flowed 64 brl of 30° oil in 15 hr from the M–Frio. C. A. F.

1613. Progress report : Portilla field. J. A. Kornfeld. *Oil Gas J.*, 4.1.51, **49** (35), 54.—The Portilla field, San Patricio County, Texas, was discovered in Feb. 1950, and current production is 6775 b.d. from nineteen wells; approx forty further locations are available. Four oil pays and one gas-condensate pay have been found, ranging from 7000 to 8100 ft in the Oligocene Frio. Most wells have been dually completed in reservoirs at 7400 and 8100 ft. Gravity varies from 39·1° to 60·6°.

Gas is to be returned to the reservoirs at 5000 to 7000 M.c.f/day. C. A. F.

1614. Scurry field has 2½ billion brl. Anon. *Oil Gas J.*, 23.11.50, **49** (29), 88.—A material balance calculation on the Kelly–Snyder field, West Texas, gave 2400 million brl of stock tank brl oil originally in place, compared with 2760 million brl determined volumetrically.

Data used in the calculation are given. C. A. F.

1615. Leduc D–3 zone pool. J. E. Baugh. *World Oil*, Mar. 1951, **132** (4), 210.—Approx 306 wells have been completed in the D_3 zone in the Leduc field, Alberta, and it is estimated that 450 to 475 additional wells will be required to drill up the pool.

The D_3 is a local high on a large reef whose areal extent is unknown. The rock is a dolomite with intergranular and cavernous porosity, averaging 13%. There is some fracturing. The max oil column is 38 ft above oil–water level, and there is a large gas cap overlying the oil zone. The original reservoir pressure was 1894 p.s.i.g. at 2980 ft subsea and 152° F. Crude averages 39° API. Recoverable reserves of the D_3 are estimated at 175 to 200 million brl.

A cross-section of the Leduc field, a representative electric log of the pay zone, and a bottom-hole pressure-decline curve for the D_3 are included. C. A. F.

1616. France's Lacq field. Anon. *Oil Gas J.*, 21.12.50, **49** (33), 283.—Seven wells had been completed in the Lacq field in southwestern France by the end of Sept. 1950. Six of these were producers, of which four were flowing and two pumping. Daily field production averages 350 metric tons, containing approx 1·3% water. Pay is Campanian limestone, which varies from marly to crystalline and fractured. Wells producing from the fractured limestone have a larger potential than those in the marly zone. The oil is undersaturated, and there is no gas cap.

The crude is naphthenic–paraffinic, containing 3·89% sulphur and 3·1% paraffin. It is refined at Pauillac. C. A. F.

1617. Wildcatting and refinery modernization highlight activity in Trinidad. Anon. *Oil Gas J.*, 21.12.50, **49** (33), 297.—There is a general trend towards deeper production in Trinidad, the deepest well being 10,500 ft. Production has shown little decline over the last three years, but there has been a continued fall in the proportion of flowing production.

There are three main objectives in the current exploratory programme. These are: the distribution of the Oligocene (Herrera) sands across the island south of the Central Range, Eocene and Cretaceous prospects north of the Central Range, and Cretaceous prospects south of the Central Range.

Marine gravity surveys have been carried out.

Drilling and production practice, and refinery developments are briefly described. C. A. F.

1618. Oil and gas developments in Bahrein Island, Saudi Arabia, and Qatar during 1949. J. T. Duce and N. E. Baker. *Petrol. Tech.*, Dec. 1950, **11** (12), 400–3.—In 1949 Bahrein produced 10,985,484 brl of oil. Two wells were completed. Saudi Arabia gave 174,008,629 brl (138,080,401 brl from Abqaiq). Twenty-four wells were completed including successful wildcats at Haradh and Fadhili.

Tables present production and drilling data, and information on wildcats. G. D. H.

1619. Germany's 1950 oil output tops 7·8 million brl. Anon. *World Oil*, Mar. 1951, **132** (4), 224.—Production in Western Germany in 1950 exceeded 7·8 million brl, or approx 32% more than 1949 production.

More than 3·5 million brl were produced from the Emsland area, which has reserves estimated at 187 million brl. The Hanover field produced about 3·4 million brl in 1950. C. A. F.

1620. Pakistan activity quickens. Anon. *World Oil*, Mar. 1951, **132** (4), 208.—Preparations are being made for drilling in the Patharia Forest of East Pakistan. Previous work in the area showed evidence of folding, and a number of good oil shows were found.

As a result of the Chakwal 2 Sakesar discovery, another well was drilled in West Punjab. This produced only small quantities from the Sakesar after shooting and acidizing.

Balkassar 4, in West Pakistan, found a high-pressure water zone at 5900 ft, and was deepened to the Sakesar.

Seismic work has been carried out in the Chak Naurang area, where a wildcat is to be drilled this year.

Approx 1,500,000 brl were produced in Pakistan in 1950, compared with 560,000 brl in 1948. C. A. F.

1621. Our oil and gas reserves—their meaning and limitations. F. H. Lahee. *Oil Gas J.*, 30.11.50, **49** (30), 69.—The terms used in discussing oil reserves must be exactly defined, and the term " recoverable reserves " should be used in referring to reserve estimates.

The percentage of oil which can be produced is the " recovery factor," and the total amount of oil estimated to have been originally in place is the estimated " total ultimate " yield.

Recoverable reserves of oil remaining under drilled units are " drilled proved reserves," and undrilled areas closely related to the drilled units are " undrilled proved reserves."

In the data published by the API for proved reserves under " new discoveries," the quantity of new reserves to be subsequently proved by drilling and added to the proved reserves of newly discovered fields in any given year is underestimated. C. A. F.

Transport and Storage

1622. The twin-screw motor tanker " Irland." Anon. *Motor Ship*, Apr. 1951, **32** (373), 24.—Description and illustrations are given of first large post-war German-built ship, 14,500-ton tanker " Irland," launched in Oct. 1950. Ship has thirty cargo tanks for carriage of oil, of capacity 673,590 cu. ft., with a dry cargo hold of capacity 35,281 cu. ft. Capacities of fuel oil and heavy oil tanks are 1027 and 467 tons respectively. Propelling machinery consists of two single-acting two-stroke 2550-b.h.p. M.A.N. engines of stroke 900 mm and bore 520 mm. Speed is 166 r.p.m., and corresponding combined output is 5100 b.h.p. or 5800 i.h.p. Engines are fresh-water cooled. U. M.

1623. Flow conditions in large diameter crude lines. L. E. Anderson. *World Oil*, Oct. 1950, **131** (5), 197.—The recent increase of large-dia pipelines, termed " big inch," of dia above 16 inch, has necessitated investigation into the conditions existing in this range. It is generally agreed that the knowledge gained in the use of small-dia pipes may not be accurately applied to " big inch " flow. The importance of optimum size selection, both from the standpoint of economy, and from that of safety, cannot be over-emphasized.

The pressure drop over a length of pipe is a function of the constants of the pipe and the fluid, of the delivery rate, and of a dimensionless friction factor. The accuracy of the latter determines the use of the equation of flow; greater difficulty is found in its estimation in the turbulent region. Tests were conducted on sections of pipelines, to obtain more accurately the relevant data. Pressures were checked by dead-weight gauges; rate of flow metered in tanks; uniform pipe dia ensured by scraping the pipe.

Inaccuracies would arise with large ratios of dia/thickness, owing to lack of circular sections, and with corroded pipe.

Various equations for use in the turbulent region are considered. The variation of visc of oil under pressure and temp changes were also mentioned. A. J. H.

1624. Radio-active tracers in products handling. R. P. Howell and R. K. Bond. *World Oil*, Nov. 1950, **131** (6), 208.—Increased use is being made of radioactive tracers in locating interfaces of individual stocks transported in one pipeline. The system of transportation of batches of liquid is not new, but the introduction of radioactive tracers increases the convenience and accuracy of separation. These points are emphasized in the case of lines handling relatively small amounts of individual products, and having several take-off points.

Preparation and injection of the isotopes are explained. The system is quite safe, as both dilution and decrease in radioactivity occur soon after injection; very small quantities are needed for tracing interfaces. A. J. H.

1625. Deep water pipeline design and construction. E. Sterrett. *World Oil*, Nov. 1950, **131** (6), 199.—Description is given of the method adopted to link the Gulf of Mexico production with the shore, by the laying of 8-inch pipeline. The line was assembled in 1100-ft sections, sufficient pipe being launched in one operation to enable another unit of 1100-ft line to be welded on. The longest section handled was 6600 ft. Buoyancy was increased by the attachment of oil drums under air pressure.

A simple operation in principle, it was confused by the effects of wind and current. A. J. H.

1626. Concrete-coated pipe for swampy terrain. A. Gibbon. *World Oil*, Nov. 1950, **131** (6), 247.—Initial fears of the practicability of concrete-coated pipe have been unfounded, as demonstrated by the successful application of this pipe. The concrete allows for the use of thin-walled pipe, giving it surface protection and improving line anchorage in swampy regions by its increased weight. The concrete overlays a corrosion-protective coating and galvanized wire mesh which acts as a base reinforcement. A turntable fitted with twelve studs holds the 12¾-inch O.D. pipe in the vertical position while concrete is applied by an ascending hopper. Thirty min are allowed before removing the coated pipe and laying it out for overnight hardening. A. J. H.

1627. Tapline pump stations and terminal. Anon. *World Petrol.*, 1951, **22** (1), 36–8.—Six stations have been established between the terminals of Tapline. At Abqaiq, steam drives two 6000-h.p. turbines coupled to two-stage centrifugal pumps operating at 3600 r.p.m., each capable of delivering 340,000 b.d. against a max of 840 p.s.i. At each of other five stations there are five (four operating, one stand-by) 8-cyl 1710-h.p. diesel engines driving single-stage pumps operating at 2200 r.p.m. Crude oil is used as fuel. At each station there is a 96,000-b.d. crude tank, and at the Sidon terminal sixteen 180,000-brl floating-roof tanks, three of which are used for bunker fuel. Gravity feed to four berths is at rate of 90,000 brl/hr. E. B.

1628. Tapline completed. Anon. *World Petrol.*, 1951, **22** (1), 30–5.—Description of the construction of the $230 million 1068-mile pipeline from Abqaiq to Sidon. Operation of the line has released sixty-five T2 tankers and reduced the price of crude by about 70c/brl. Delivery capacity of the line with six pumping stations is some 300,000 b.d., with potential capacity of 500,000 if six more pumping stations are added. Dead storage of the line is about 5 million brl, and a further 1½ million brl is required at pumping stations and terminals. All material and equipment was imported, storage space being saved by having alternate joints of pipe 30- and 31-inch dia, nesting the smaller in the larger. About 60% of the length is buried. The remainder is supported above the ground at 66-ft intervals. E. B.

1629. Slack loop practice in lowering-in procedure. T. B. La Rock. *World Oil*, Nov. 1950, **131** (6), 220.—A temp range of 100° F atmospheric conditions to 40° F at pipe level had necessitated the introduction of "slack" in the 30-inch transmission line laid in New Mexico. The operating company maintained that max welding efficiency had been attained in previous cases, and failure in those lines was therefore attributed to lack of "slack."

The slack loops, which are placed every 1000 ft, approximated to sine curves of 2·5 ft amplitude and 400 ft wavelength, thereby introducing 2 inch of slack per loop. Stress and temp conditions were carefully observed. The procedure is described, and details of the operating conditions given. A. J. H.

1630. Magnetic scraper locator. J. W. Jones. *World Oil*, Oct. 1950, **131** (5), 202.—The position of a magnetized scraper may be easily determined with the equipment described. The advantages of this magnetic detector over other methods, audible detection or detection by Geiger–Müller counter, are given. Little experience is required by the operator to distinguish between buried metal objects and the magnetic scraper in the buried line. A. J. H.

1631. Pipeline crossing uses jacketing of barytes-laden cement. J. A. Kornfeld. *Oil Gas J.*, 12.4.51, **49** (49), 82.—An installation employing barytes-weighted concrete in a river crossing of 24-inch, ½-inch wall pipe at Wallis, Texas, is described; the concrete jacketing being applied by pneumatic pressure. The wt additive is barium sulphate, added with equal wt of sharp sand, a 4 : 1 ratio cement to mixture being used. The method eliminates need for river clamps, ballasting is improved, and pipe life lengthened. G. A. C.

1632. Richfield's Cuyama Valley L.P.G. loading racks. M. L. Arnold. *Oil Gas J.*, 19.4.51, **49** (50), 151.—New flow layout for loading L.P.G. into tank-trucks is described and compared with old system, flow sheets of both designs being shown.

Procedure for loading is given in full as issued to operators.

Safety devices are installed, for example, if the loading valves are opened but one hose is left uncoupled or loosely coupled, the rack cannot be put into operation.

Loading now required only from 30 to 45 min, depending on size of truck.

G. A. C.

1633. Gauging of horizontal elliptic cross-section tanks with dished ends. J. Breuil. *Chim. et Ind.*, 1951, **65**, 501–7.—Nomograms are derived and reproduced covering the range (metres) height 10, large axis 15, small axis 10, length 20, depth of dished ends 1. Accuracy (as compared to calculation) is better than 2%. (Cf. Abstract No. 1030, 1950.) V. B.

1634. Underground storage tanks. W. F. Matheny and G. H. Billue. *Chem. Engng*, 1950, **57** (12), 115.—It has been demonstrated that hydrocarbon liquids can be satisfactorily stored in underground cavities made by dissolving parts of salt strata with water. A bore hole is made and lined with two concentric pipes. Water pumped down will dissolve salt until saturated, and by pumping hydrocarbon in, brine is displaced. One experimental cave of 7000 brl cost $2·50—one-seventh of above-ground steel storage. D. H.

1635. Handling carbon black: Recommendations on stowage. Anon. *India-Rubber J.*, 1951, **120** (16), 624.—A brief review is given of British Standard 1714 (Part 1) entitled "British Standard Recommendations for Handling Carbon Black: Loading and Stowing in Ships." Suggestions are made relating to stowage space, preparation of holds, loading, and stowing. Further recommendations will cover land transport and minimum-quality standards for packaging. C. N. T.

Refinery Operations

Refineries and Auxiliary Refinery Plant

1636. Design of packed absorption and distillation columns. II. H. R. C. Pratt. *Industr. Chem.*, 1950, **26**, 470–4.—Dia of packed dist column is satisfactorily based on vapour velocity of 55 to 70% of flooding rate. Separate formulæ covering rectifying and stripping sections of columns are given. Min value of flooding rate frequently occurs at base of stripping section, but when light component has higher mol. wt. it may occur at top of rectifying section; this is also usually the case with vac columns. If vapour velocity less in practice than calc, lower column performance results because

of reduced wetted area of packing. Methods of calculating column heights for binary and multi-component systems are given, based on H.E.T.P. and on height of a transfer unit. Allowances calc for deviations from usual simplifying assumptions due to differences in molar lat. ht. of vaporization of components. Greater number of transfer units then required, but difference is comparatively small. Safety factor of 20 to 25% above calc packed height recommended to allow for liquid distribution effect. (Cf. Abstract No. 2120, 1950.) A. C.

1637. Design of packed absorption and distillation columns. III. H. R. C. Pratt. *Industr. Chem.* 1951, **27**, 3–8.—Curves shown illustrating influence of variations in throughput on performance of typical dist columns packed with various sizes and types of packing. Values of H.E.T.P. and height of a transfer unit-calc for vapour velocities varying from 10 to 80% of min flooding rate, and optimum vapour velocity shown to be 60 to 65% of flooding rate. In general 1-inch Raschig rings are most satisfactory packing. Advantages and limitations of packed dist columns are discussed, and max permission dia of packed column given as 2 ft 6 inches to 3 ft 0 inches. Practical design problems considered include: (*a*) conveniences of shell construction in standard sections of 10 to 15 dia long (max 15 ft), (*b*) packing supports which should have min 75% free space compared with packing, (*c*) introduction of wall liquid redistributors, (*d*) reflux distribution plates using standard carburettor jets, (*e*) multiple-feed inlet pipes drilled in upper side, (*f*) split-box for R.F.R. control, using standard weir formula and assuming min head of ¼ inch. Instrumentation is illustrated by typical two-unit packed-column vac dist plant, with particular reference to care required in close control of packed columns because of low hold-up in packing. A. C.

1638. Design of packed absorption and distillation columns. IV. H. R. C. Pratt. *Industr. Chem.*, 1951, **27**, 51–8.—Two worked examples are given, one a design for a typical absorption column where both film resistances are appreciable (recovery of acetone vapour from air by scrubbing with water), and the other a design for a continuous dist column separating a binary non-ideal mixture (acetone/water). In both cases a safety factor of about 20% above theoretical is applied. **V.** *ibid.*, 1951, **27**, 152–6. Two further examples are worked out, the first relating to design of a continuous distillation with a ternary ideal system (benzene/toluene/xylene), and the other a calculation of a batch dist curve. A. C.

1639. How to apply removable insulation over process vessel. M. A. Allen. *Chem. Engng*, 1950, **57** (10), 155.—A convenient method of insulating welded vessels is described. Removable panels are incorporated over the welds so that inspection does not necessitate removal of the entire insulation. Expansion in two directions is allowed for. D. H.

1640. Cooling towers. J. C. Theron Mulder. *Ingenieur*, 9.3.51, **63** (10), Ch. 9.—The influence on cooling-tower performance of various factors is briefly discussed, and this is followed by a breakdown of the conditions obtaining in various parts of the tower. The article further describes, with appropriate mathematical constructions, the water loading, the heat and material interchange, and cooling and resistance characteristics. These factors can be characterized by means of dimensionless numbers, and their interdependent functions may be determined by experiment. A number of graphs are included to demonstrate the relationship between the factors concerned. R. R.

Distillation

1641. Gladewater puts Perco unit in operation. H. A. Grebe, A. L. Miles, and K. W. Seed. *Oil Gas J.*, 12.4.51, **49** (49), 80.—The New Perco Cycloversion unit of Gladewater Refining Co., Texas, is designed to process 650 b.s.d. of either cracked gasoline, straight-run naphtha, or blends of these two products.

Unit is mounted on three skids, except for heaters. Tables show catalytic desulphurization of thermal-cracked gasoline and catalytic reforming of straight-run naphtha, and a flow sheet for gasoline upgrading is given. G. A. C.

1642. Snyder gasoline plant designed to process 70,000 M.C. of gas daily. H. W. Manley. *Oil Gas J.*, 19.4.51, **49** (50), 174.—The new Snyder natural-gasoline plant owned by thirty companies in the Scurry Country, Texas, is described. Gas will be gathered from 850 wells, the 70,000 M.c.f/day of gas is brought into the plant by two complete systems for low and high pressures.

Propane, butane, *iso*butane, and 18-lb R.V.P. gasoline are products, yields being 230,000, 137,000, 38,000, and 142,000 gal/day respectively. G. A. C.

Cracking

1643. Platforming. Anon. *Chem. Engng*, 1950, **57** (10), 172–5.—Basic principles are set out, and a typical flow sheet is provided. D. H.

1644. Catalyst life greater than expected. Anon. *World Petrol.*, 1951, **22** (2), 35–7.—On Old Dutch Platforming unit, catalyst life of 42 brl of feed/lb has been found on normal operation, thus exceeding estimated 32 brl/lb. Cost of catalyst is 9c/brl of feed. A report is given of fifteen months' running. E. B.

Hydrogenation

1645. How Lookout Oil gets H_2 for its hydrogenation operations. E. D. White. *Chem. Engng*, 1950, **57** (9), 104–6.—The cost of electrolytic hydrogen (H_2) near T.V.A. is 0·8c per 1000/cu. ft. A new process provides 99·95% H_2 with 20% overall saving in costs. The electrolytic process has the disadvantage of having to find markets for oxygen.

Propane and steam react at 1700° F with Ni catalyst to produce H_2, CO, and CO_2. CO is converted to CO_2 in three stages and CO_2 removed by Girbotol process (mono-ethanolamine absorption). Sulphur is removed from propane before reaction by scrubbing with NaOH.

Final impurities are: 0·001% O_2; 0·005% CO; 0·005% CO_2; methane and inert 0·039%. Capacity of plant is 150,000 cu. ft/day. D. H.

Chemical and Physical Refining

1646. More heating facilities being completed at Chesterville, Tex, gasoline plant. F. L. Resen. *Oil Gas J.*, 19.4.51, **49** (50), 161.—A treating system to remove hydrogen sulphide from the propane system is nearing completion. The plant serves several fields in the Colorado County section of Gulf Coast area. System includes a caustic scrubber and two driers installed between depropanizer and propane storage. Present throughput is 40,000,000 cu. ft/day of wet gas from which is extracted 99% of the pentanes, 95% of the butanes, and 30% of the propane. G. A. C.

1647. Sodafining. M. C. K. Jones. *Oil Gas J.*, 12.4.51, **49** (49), 88.—Raw gasoline from fluid catalytic cracking processes using heavier higher sulphur feeds is less stable, and the instability is avoided by application of a process involving controlled caustic washing before exposure to air. This removes aromatic mercaptans and reduces peroxidation and gum formation.

The process, "Sodafining," has been developed by Standard Oil Co.

Tables give inspection data on various naphthas before and after treatment.

G. A. C.

1648. Practical and economic heating system for an average gasoline plant. G. M. Brooner. *Oil Gas J.*, 19.4.51, **49** (50), 184.—Treating systems for a gasoline plant producing propane, butane, and grade natural gasoline, to remove hydrogen sulphide, free sulphur, and mercaptans are discussed.

Basic requirements for such plants include elimination of hydrogen sulphide as early as possible to prevent equipment corrosion and production of specification doctor-sweet and non-corrosive products. Flow sheets are given.

G. A. C.

Special Processes

1649. A new dephenolization process for low-temperature carbonization plants. W. Lowenstein-Lom. *Petroleum*, Feb. 1951, **14** (2), 33–5.—From the point of view of river pollution the removal of phenols is by far the most important of the various purification processes. Author shows that, particularly in the presence of organic bases, certain solvent fractions can be used and are preferable to benzole and solvents obtained by high-temp tar distillation. Ammoniacal liquor dephenolization in the actual plant is effected by first passing it through a Schumann tar separator, to break up the oil emulsions. It then enters the top of a 6-ft-dia 40-ft-high extraction tower filled with Raschig rings, and leaves through a swan-neck level regulator. Straw oil, dephenolized in a caustic soda scrubber and washed with water, is pumped into the bottom of the extraction tower, and, when saturated with phenols, is returned from the top of the tower to the alkaline scrubber. The liquor after dephenolization, with some dispersed oil, flows through a sand filter to a storage tank.

Concentration of phenols in the plant effluent is of the order 0·2 g/litre, and 95% of the phenols in the liquor are extracted. No biological treatment was required. Boiler ash from the power-station was washed down by means of the liquor, reducing concentration to 10 to 15 mg/litre. Further dilution by other plant effluents and river-water brought this down to below 1 p.p.m. R. E. P.

1650. More carbon black. Anon. *Petroleum*, Mar. 1951, **14** (3), 67–8.—The Philblack carbon-black plant stated to be the largest plant of its kind outside the U.S., is described. Scheduled to produce 50,000,000 lb of carbon black p.a., the plant is due to go into production early in 1951.

Raw material is a special petroleum fraction; 70,000 tons p.a. will have to be imported to keep the plant in full operation. It is stated that the ideal raw material should contain a max of aromatics, be low in sulphur, be substantially free from suspended ash or carbon, be low in high-mol.-wt. resins and asphaltenes, and substantially free from emulsifying water.

Two grades will be produced. *Philblack "A"* designed for use in extruded rubber products and *Philblack "O"* a high abrasive-resistant black for tyres. The process consists of careful burning of oil, with partial exclusion of air and the separation of carbon black from the combustion products using electrostatic precipitation, cyclone collectors, and a bag filter unit. Carbon black produced is pulverized and pelleted to minimize dust problems in subsequent handling. R. E. P.

Metering and Control

1651. Control of multiple effect evaporators. A. C. Camp and L. E. Slater. *Chem. Engng*, 1950, **57** (9), 108–11.—The chief variables are quality and density of incoming liquor; first effect steam pressure; last effect vacuum; amount of vapour bled off for heating purposes. The basic control problem and instruments required are summarized. Methods available for level control and density controls are detailed. D. H.

1652. Electronic control. Anon. *Petroleum*, Feb. 1951, **15** (2), 40–2.—Describes briefly the principles of electronic control and some interesting special applications. Applications include many types of welding control, measurement of time, visc, pH by glass electrodes, temp, etc., gas analysis, strain gauges, and instruments for recording changes in the stress due to vibration. R. E. P.

Products

Chemistry and Physics

1653. Absorption spectra and photo-isomerization of arylated dienes. Y. Hirshberg, E. Bergmann, and F. Bergmann. *J. Amer. chem. Soc.*, 1950, **72**, 5120–3.—A number of substituted 1 : 4-diphenylbutadienes were examined spectrographically to determine the effects substituents exert on the ability of the molecule to resonate. It is concluded

that substitution which causes steric interference around the double bonds can cause a shift of the largest absorption maximum of 1 : 4-diphenylbutadiene towards the ultra-violet, a disappearance of fine structure, and a lowering of the extinction coefficient. It is confirmed that all *trans-trans* compounds are stereoisomerized by ultra-violet light. W. H. A.

1654. Adsorption of benzene and *cyclo*hexane by graphite. R. N. Smith, C. Pierce, and H. Cordes. *J. Amer. chem. Soc.*, 1950, **72**, 5595–7.—Adsorption isotherms are given for benzene and *cyclo*hexane on Graphon, a partially graphitized carbon black, at 5·5° and 28·6° C. It is reported that the area covered per mol is approx 38 Å for *cyclo*hexane and 41 Å for benzene, indicating that the mols lie flat on the surface. It is concluded that the isotherms and isosteric heats of adsorption calculated from them indicate *cyclo*hexane to be more strongly adsorbed than benzene in the first layer, and benzene to be the more strongly adsorbed in the multi-layer region. W. H. A.

1655. An azeotrope between paraffin hydrocarbons. G. Calingaert and M. Wojciechowski. *J. Amer. chem. Soc.*, 1950, **72**, 5310–11.—Deviations from ideality are reported between paraffin hydrocarbons and even between isomeric paraffins. Examination of the binary system 2 : 2 : 3-trimethylbutane/2 : 4-dimethylpentane produced evidence of the existence of negative azeotropy in the system. W. H. A.

1656. Chemical characterization of catalysts. II. Oxygen exchange between water and cracking catalysts. G. A. Mills and S. G. Hindin. *J. Amer. chem. Soc.*, 1950, **72**, 5549–54.—The exchange of oxygen between water and silica gel, alumina gel, active silica–alumina cracking catalyst, kaolin clay, bentonite clay, and acid-activated bentonite clay were measured at 100° C, and in some cases at 565° C, using an isotopic tracer technique.

The materials with large surface areas were found to take part in oxygen exchange in two stages, first a rapid exchange involving 10 to 25% of all the oxide oxygens followed by a slower exchange involving a further 10 to 60% of the oxide oxygens.

Natural kaolin and bentonite undergo no apparent change, which it is suggested may be due to their comparatively low surface area and their crystalline structure. A mechanism of oxygen exchange is discussed. W. H. A.

1657. Cation complexes of compounds containing carbon–carbon double bonds. VI. The Argentation of substituted benzenes. L. J. Andrews and R. M. Keefer. *J. Amer. chem. Soc.*, 1950, **72**, 3113–16.—Equilibrium constants for the formation of water-soluble complexes $AgAr^+$ and Ag_2Ar^{++} have been calculated from the solubilities of some mono- and di-substituted benzene derivatives (Ar) in aqueous silver nitrate at 25° C. The relative magnitudes of the argentation constants have been discussed in terms of Hammett's ρ, σ substituent complexes, and it is suggested that the structures of the complexes are similar to those of intermediates in aromatic substitution reactions. W. H. A.

1658. Cation complexes of compounds containing carbon–carbon double bonds. VII. Further studies on the argentation of substituted benzenes. L. J. Andrews and R. M. Keefer. *J. Amer. chem. Soc.* 1950, **72**, 5034–7.—Equilibrium constants at 25° C for the formation of argentation complexes of the type $AgAr^+$ have been determined for several benzene derivatives. It has been found that the argentation constants for a number of mono-alkylbenzenes are comparable to those obtained for benzene and toluene. Styrene readily forms a complex with silver ion, and it is suggested that the vinyl side-chain acts as the electron donating part of the organic molecule. In contrast to its behaviour in other reactions where the aromatic nucleus acts as an electron donor, mesitylene is a weaker base than benzene or xylene, and it is possible that this may be attributed to steric effects associated with the methyl groups which inhibit argentation. Ethyl cinnamate, 1 : 1-diphenylethylene, and *trans*-stilbene show a much lower activity in the argentation reaction, and this is discussed in terms of steric and electronic effects. W. H. A.

1659. Cyclic polyolefins. VII. Structure of the eight-membered cyclic dimer of chloroprene. A. C. Cope and W. R. Schmitz. *J. Amer. chem. Soc.*, 1950, **72**, 3056–62.—The structure of the eight-membered cyclic dimer, which is formed together with two six-membered dimers when chloroprene is allowed to stand or is heated in the presence of polymerization inhibitors, has been established as 1 : 6-dichloro-1 : 5-*cyclo*-octadiene by identification of the degradation products obtained following ozonization. Confirmatory evidence was afforded by identification of the unsaturated ketone resulting from the treatment of the eight-membered dimer with concentrated sulphuric acid. This ketone was shown to be bicyclo-(3 : 3 : 0)-1 (5)-octen-2-one. W. H. A.

1660. Cyclic polyolefins. IX. Synthesis from carbonyl-bridged intermediates. 2 : 4-Diphenyl*cyclo*-octa-1 : 4-diene. A. C. Cope, F. S. Fawcett, and G. Munn. *J. Amer. chem. Soc.*, 1950, **72**, 3399–405.—The synthesis of substituted unsaturated eight-membered ring compounds by removal of the carbonyl bridge in compounds containing the bi*cyclo*-[3 : 3 : 1]-nonan-9-one ring system has been demonstrated. Subjecting the oxime of 2 : 4-diphenylbi*cyclo*-[3 : 3 : 1]-non-2-en-9-one to the Beckmann re-arrangement resulted in rupture of the carbonyl bridge with the formation of a lactam. Acid hydrolysis of the lactam followed by exhaustive methylation by the method of Hofmann produced 2 : 4-diphenyl*cyclo*-octa-1 : 4-diene. Study of the ultra-violet absorption spectra of a number of compounds in this series produced information on the position of the double bonds. W. H. A.

1661. Cyclic polyolefins. X. Synthesis of phenyl*cyclo*-octa-1 : 3-diene. A. C. Cope and E. C. Hermann. *J. Amer. chem. Soc.*, 1950, **72**, 3405–10.—A phenyl*cyclo*-octa-1 : 3-diene was prepared from *cyclo*hexanone and β-dimethylaminopropiophenone which yielded the carbonyl-bridged compound 2-phenylbi*cyclo*-(3 : 3 : 1)-non-2-en-9-one. The oxime of this cyclic ketone was subjected to the Beckmann re-arrangement and hydrolysis, followed by exhaustive methylation of the resulting lactam. Thermal decomposition of the quaternary base yielded the phenyl*cyclo*-octa-1 : 3-diene, which was shown to contain an unbridged eight-membered ring by quantitative hydrogenation to phenyl*cyclo*-octane. W. H. A.

1662. The fluorescence of 1 : 4-diarylbutadienes and its relation to their configuration. Y. Hirshberg, E. Bergmann, and F. Bergmann. *J. Amer. chem. Soc.*, 1950, **72**, 5117–18.—The fluorescence spectrum of some arylated butadienes has been measured, and it is concluded that fluorescence requires an extended resonating system as indicated by the more intense fluorescence of *trans-trans*-isomers compared with *cis-trans*-isomers and the observation that substituents which extend the resonating system in 1 : 4-diphenylbutadiene increase the intensity of fluorescence. Prolonged irradiation caused a decrease in fluorescence intensity due to re-arrangement of *trans-trans*-forms. W. H. A.

1663. The purification and some physical properties of *cyclo*octatetraene. B. H. Eccleston, H. J. Coleman, and N. G. Adams. *J. Amer. chem. Soc.*, 1950, **72**, 3866–70.—The purification of *cyclo*octatetraene and the apparatus used is described. Data on the density, visc, refractive index, and the ultra-violet and infra-red absorption spectra of the purified sample are given, as are equations relating visc–temp, density–temp, and refractive index–wavelength over the ranges investigated. W. H. A.

1664. Bicyclic hydrocarbons. I. 2-Alkylbiphenyls. I. A. Goodman and P. H. Wise. *J. Amer. chem. Soc.*, 1950, **72**, 3076–9.—In an investigation of the possible components of aviation fuel, five 2-substituted alkyl biphenyls have been synthesized. The series consists of biphenyls substituted in the 2-position by the radicals : methyl, ethyl, propyl, *iso*propyl, and butyl and their preparation, purification, and physical constants are recorded. With the exceptions of the 2-methyl and 2-ethyl derivatives, they have been described for the first time. W. H. A.

1665. Hydrogen transfer. V. Reaction of *m*-cymene and *o*-cymene with methyl*cyclo*-hexene in the presence of hydrogen fluoride. H. Pines, D. R. Strehlau, and V. N. Ipatieff. *J. Amer. chem. Soc.*, 1950, **72**, 5521–3.—Pure *m*-and *o*-cymene were prepared

and treated with 4-methyl*cyclo*hexene at 0° C in the presence of anhydrous hydrogen fluoride. The *m*-cymene underwent a hydrogen-transfer reaction, producing 1 : 3 : 3 : 5-tetra-methyl-l-*m*-tolylindan, and a *cyclo*alkylation reaction which predominated. In the case of *o*-cymene only *cyclo*alkylation occurred. W. H. A.

1666. Hydrocarbons. XI. Synthesis of nineteen decenes. C. J. Stehman, N. C. Cook, W. C. Percival, and F. C. Whitmore. *J. Amer. chem. Soc.*, 1950, **72**, 4163–5.—Six tertiary decanols were prepared and dehydrated over alumina, and by fractionation of the dehydration mixture nineteen decenes were obtained. These were characterized by boiling point, refractive index, Raman spectra, density, and visc, and their structure elucidated by ozonolyses. Dehydration products were predominantly unre-arranged, with ethylidene compounds being most readily formed, and if these could not be produced without re-arrangement, then methylene olefins predominated. Only small quantities of olefins with double bonds between tertiary carbon atoms were produced. W. H. A.

1667. Isomerization accompanying alkylation. VI. Reaction of *iso*butylene and 2-butene with benzene. H. Pines, J. D. LaZerte, and V. N. Ipatieff. *J. Amer. chem. Soc.*, 1950, **72**, 2850–3.—The catalytic alkylation of benzene with butylenes at high pressures and elevated temp was investigated with the object of determining if alkylation was accompanied by isomerization of the alkyl group. Benzene was treated with 2-butene and also with *iso*butylene in the presence of different catalysts. A flow-type apparatus was used, and temp ranged from 200° to 380° C at a pressure of 40 atm, while the mol ratio of benzene to olefin was about 2·5 to 1·0.

Benzene and 2-butene reacted in the presence of a silicophosphoric acid catalyst, yielding a monobutylbenzene fraction containing 12 to 21% of *t*-butylbenzene as well as *s*-butylbenzene, together with higher-boiling hydrocarbons. When zinc chloride–alumina catalyst was used for the same reaction the degree of isomerization was very slight, while silica–alumina catalyst yielded only *s*-butylbenzene. The reaction of benzene with *iso*butylene using silico-phosphoric acid catalyst also resulted in a mixture of *s*-butylbenzene and *t*-butylbenzene.

Dealkylation of di-*s*-butylbenzene and di-*t*-butylbenzene in the presence of benzene and catalysts yielded a mixture of *t*- and *s*-butylbenzenes, while at 350° C in the presence of benzene and silico-phosphoric acid catalyst both *t*- and *s*-butylbenzenes were partly isomerized. W. H. A.

1668. Isomerization of saturated hydrocarbons. VII. The effect of light upon the isomerization of methyl*cyclo*pentane in the presence of aluminium bromide–hydrogen bromide. H. Pines, E. Aristoff, and V. N. Ipatieff. *J. Amer. chem. Soc.*, 1950, **72**, 4055–6.—Methyl*cyclo*pentane is isomerized to *cyclo*hexane in the presence of aluminium bromide–hydrogen bromide without the addition of chain initiators, by exposure to ultra-violet light.

The mechanism of the reaction is discussed, and it is shown how the *cyclo*-olefins or *cyclo*alkyl halides necessary for the initiation of an ionic chain isomerization reaction may be formed. Small amounts of benzene inhibit the reaction. W. H. A.

1669. Isomerization of saturated hydrocarbons. VIII. The effect of oxygen and light upon the isomerization of methyl*cyclo*pentane in the presence of aluminium bromide. H. Pines, E. Aristoff, and V. N. Ipatieff. *J. Amer. chem. Soc.*, 1950, **72**, 4304.—In the presence of oxygen, aluminium bromide catalysed the isomerization of methyl-*cyclo*pentane to *cyclo*hexane when the reaction mixture was exposed to a quartz cadmium–mercury arc lamp. It is suggested that the aluminium bromide is oxidized, liberating bromine, which reacts with the methyl*cyclo*pentane, forming bromo-methyl-*cyclo*pentane. The latter then acts as a chain initiator for the reaction. W. H. A.

1670. The nitrogen compounds in petroleum distillates. XXVII. Isolation and identification of 2 : 3-dimethyl-6-*iso*propylpyridine from California petroleum. H. L. Lochte, A. D. Barton, S. M. Roberts, and J. R. Bailey. *J. Amer. chem. Soc.*, 1950, **72**, 3007–9.—An aqueous solution of the hydrochlorides of bases from California petroleum were " cumulatively " extracted with chloroform, and bases boiling between 192° and 230° C were separated from the hydrochlorides in the chloroform layers. Following fractiona-

tion by sulphurous acid and fractional distillation, the methiodide was formed and recrystallized from absolute alcohol, giving the methiodide of a $C_{10}H_{15}N$ base. Analysis of the separated base by a series of degradation reactions showed it to be 2 : 3-dimethyl 6-*iso*propylpyridine. W. H. A.

1671. Olefins from alcohols. W. Brandenberg and A. Galat. *J. Amer. chem. Soc.*, 1950, **72**, 3275–6.—Olefins may be obtained in almost quantitative yield by the dehydration of alcohols, using boric acid or anhydride as catalyst. It is claimed that the method has a more general application than any of the well-known methods. A two-stage reaction mechanism is postulated involving the formation of the boric ester and its subsequent decomposition into olefin with regeneration of the catalyst.

$$3\ R.CH_2.CH_2.OH + H_3BO_3 \rightarrow B(OCH_2.CH_2.R)_3 \rightarrow 3R.CH{:}CH_2 + H_3BO_3$$

It has not yet been established if the resulting olefin has a double bond in the 1 : 2- or 2 : 3-position or is a mixture of the two isomers. W. H. A.

1672. The preparation and purification of methane-d ethane-d propane-1-d, propane-2-d, *n*-butane-1-d, *n*-butane-2-d, *iso*butane-1-d, and *iso*butane-2-d. C. D. Wagner and D. P. Stevenson. *J. Amer. chem. Soc.*, 1950, **72**, 5785.—A series of monodeutero-alkanes had been prepared from the corresponding alkyl halides by conversion to the Grignard reagent, which is purified before treating with the deuterium reagent. After purification the chemical, isomeric, and isotopic purity of the deutero-hydrocarbons were measured by the mass spectrometer. W. H. A.

1673. Preparation and reactions of methylene-*cyclo*pentane. R. T. Arnold, R. W. Amidon, and R. M. Dodson. *J. Amer. chem. Soc.*, 1950, **72**, 2871–3.—Methylene*cyclo*-pentane was obtained by pyrolysis of the purified mixture of 1-*cyclo*pentenyl acetic acid and *cyclo*pentenylidene acetic acid resulting from the alkaline hydrolysis of 1-*cyclo*pentenylacetonitrile.

When heated with paraformaldehyde at 200° C under nitrogen, methylene*cyclo*-pentane yielded 2-(1-*cyclo*pentenyl)-ethanol, and under similar conditions when heated with maleic anhydride in benzene solution in the presence of hydroquinone the olefins formed 1-*cyclo*pentenylmethyl succinic anhydride. 1-*cyclo*pentenylmethane sulphonate resulted from the low-temp interaction of a solution of methylene*cyclo*-pentane in ethylene chloride and a dioxan–sulphur trioxide slurry.

In each of these addition reactions the exocyclic double bond migrates into the five-membered ring, and it is suggested that an intramolecular ionic mechanism explains these reactions more adequately than the free-radical mechanism postulated by Farmer to account for the formation of simple adducts from unsaturated hydro-carbons and maleic anhydride. W. H. A.

1674. The reaction of chromyl chloride with olefins. S. J. Cristol and K. R. Eilar. *J. Amer. chem. Soc.*, 1950, **72**, 4353–6.—A reaction is described in which chromyl chloride reacts with olefins, forming a compound which yields a chlorohydrin on hydrolysis. *Cyclo*hexene was converted to *trans*-2-chloro*cyclo*hexanol in fair yield and aliphatic olefins of the type $R.CH : CH_2$ reacted to produce β-chloro primary alcohols in 35 to 50% yields. Possible reaction mechanisms are discussed. W. H. A.

1675. Reactions of paraffin hydrocarbons in the presence of sulphuric acid. V. I. Komarewsky and W. E. Ruther. *J. Amer. chem. Soc.*, 1950, **72**, 5501–2.—An examination of the behaviour of *n*-octane, 2 : 4-dimethylpentane, 2 : 2 : 4-trimethyl-butane, and 2 : 2-dimethylbutane in the presence of concentrated sulphuric acid at the b.p. of the respective hydrocarbons indicated this acid to be a satisfactory isomerization catalyst for liquid hydrocarbons containing at least one tertiary carbon atom. Com-pared with aluminium chloride, the loss of paraffin to the catalyst layer is very small. W. H. A.

1676. Re-arrangement of 4-methyl*cyclo*hexene during sulphuric acid-catalyzed reaction with benzene. J. Linsk. *J. Amer. chem. Soc.*, 1950, **72**, 4257–60.—It is shown that 4-methyl*cyclo*hexene is readily re-arranged by concentrated sulphuric acid, since the sulphuric acid-catalysed alkylation of benzene with 1- and 4-methyl*cyclo*hexene and 2-

and 4-methyl*cyclo*hexanol yields the same two compounds. The monoalkylation product is 1-methyl-1-phenyl*cyclo*hexane, and the dialkylation product is believed to be 1 : 4-di-(1′-methyl*cyclo*hexyl)-benzene. W. H. A.

1677. The solubility of hydrogen bromide in normal paraffin hydrocarbons. E. R. Boedeker and C. C. Lynch. *J. Amer. chem. Soc.*, 1950, **72**, 3234–6.—The solubility of hydrogen bromide in *n*-hexane, *n*-octane, and *n*-decane has been measured at 25°, 35°, and 45° C, and the heat of solution of hydrogen bromide in each solvent has been calculated. By including Fontana and Herold's data for *n*-hexane and *n*-butene, it is possible from the experimental results to predict the solubility, over a limited range, of hydrogen bromide in *n*-paraffin solvents.

The value of Henry's law constant at a given temp approaches a limiting value as the number of carbon atoms in a molecule of the *n*-paraffin solvent increases. W. H. A.

1678. Studies in the terpene series. IX. Isomerization accompanying *cyclo*alkylation of benzene. V. N. Ipatieff, H. R. Appel, and H. Pines. *J. Amer. chem. Soc.*, 1950, **72**, 4260–2.—In the presence of hydrogen fluoride the reaction between benzene and disubstituted *cyclo*hexenes involved a hydrogen shift. Dihydrolimonene, *p*-methenes, menthol, and dihydroterpineol reacted with benzene, producing 1-methyl-1-phenyl-4-*iso*propyl*cyclo*hexane. A mixture of hydrocarbons was formed when benzene reacted with 1-methyl-4-ethyl-, 1-ethyl-4-methyl-, 1-ethyl-4-*iso*propyl-, and 1-*iso*propyl-4-ethyl-*cyclo*hexanol. The phenyl group was mainly attached to the carbon atom on the *cyclo*hexyl ring, to which is attached the smallest alkyl group. W. H. A.

1679. Studies of the Fischer–Tropsch synthesis. VII. Nitrides of iron as catalysts. R. B. Anderson, J. F. Shultz, B. Seligman, W. K. Hall, and H. H. Storch. *J. Amer. chem. Soc.*, 1950, **72**, 3502–8.—When the iron in reduced synthetic-ammonia-type catalysts is converted to nitride by ammonia treatment the catalysts have a longer life, greater stability, and appear to resist oxidation and deposition of free carbon. It is suggested that the increased activity of nitrided catalyst may be due in some part to the lower-molecular-weight products obtained, since it is expected that these are desorbed more readily, thereby increasing the effectiveness of the surface. However, a catalyst partially nitrided to γ' phase had a greater activity than a similar reduced catalyst, though the products were essentially the same. In this case the enhanced activity is not due to the nature of the products but to some specific change in the catalyst surface. Conversion to ε-phase nitride produced catalysts which showed the greatest increase in activity. The ε-phase nitrides have the same crystal structure as Fe_2C, and it is suggested that their activity is due to the arrangement and spacing of the iron atoms in these structures. During synthesis the nitrides are gradually converted to carbonitrides with the ratio of total carbon plus nitrogen to iron remaining almost constant, and it is possible that the active surface may possibly be carbide. W. H. A.

1680. Studies of the Fischer–Tropsch synthesis. VIII. Surface area and pore volume studies of iron catalysts. W. K. Hall, W. H. Tarn, and R. B. Anderson. *J. Amer. chem. Soc.*, 1950, **72**, 5436–43.—A precipitated Fe_2O_3–CuO–K_2CO_3 catalyst and a fused Fe_3O_4–MgO–K_2O catalyst have been studied. It was found that the surface area of precipitated iron-gel catalysts are high and their pore diameters small, while the fused synthetic-ammonia-type catalysts have essentially no surface area and no pore volume. Following reduction at 300° and 450° to 550° C respectively, both types of catalyst have surface areas of about 8 sq. m/g and pore dia of 350 to 900 Å. Increasing the temp of reduction of the synthetic-ammonia-type catalyst from 450° to 650° C caused an eightfold increase in the pore dia. It is stated that surface-area measurements and complete chemical analysis of the raw catalyst are sufficient to establish the pore structure of the synthetic-ammonia-type catalyst as a function of the extent of reduction. W. H. A.

1681. Structures of the OXO aldehydes from styrene. L. A. Wetzel, C. H. McKeever, and C. L. Levesque. *J. Amer. chem. Soc.*, 1950, **72**, 4939–40.—In the OXO reaction styrene yields phenyl propionaldehyde, which was shown to be 2-phenylpropionalde-

hyde by conversion to the semicarbazone. There was evidence of the presence of another semicarbazone which was not identified. Oxidation of the propionaldehyde yielded a mixture of acetophenone and 3-phenylpropionic acid, which indicates the presence of 2- and 3-phenylpropionaldehyde in the OXO reaction product.

W. H. A.

1682. Chemistry of the OXO and related reactions. II. Hydrogenation. I. Wender, R. Levine, and M. Orchin. *J. Amer. chem. Soc.*, 1950, **72**, 4375–8.—The reduction of aldehydes and ketones to alcohols by hydrogen and carbon monoxide (synthesis gas) in the presence of a cobalt catalyst is described. The reaction can also be applied to the reduction of compounds containing sulphur. A free radical mechanism for the reduction reaction is discussed. Olefins when treated with synthesis gas in the presence of a cobalt catalyst at pressures of 150 to 300 atm and between 180° and 185° C yield alcohols containing one carbon atom more than the olefin as principal products. In some compounds under these conditions the double bond is hydrogenated rather than hydroformylated.

W. H. A.

1683. The synthesis of carbon-isotopic alkanes. Methane-C^{13}, propane-1-C^{13}, *n*-butane-1-C^{13}, *n*-butane-1-C^{14}, *iso*butane-1-C^{13}, *iso*butane-1-C^{14} and *iso*butane-2-C^{13}. C. D. Wagner, D. P. Stevenson, and J. W. Otvos. *J. Amer. chem. Soc.*, 1950, **72**, 5786.—Reaction schemes for the synthesis of some isotopic hydrocarbons containing C^{13} and C^{14} are outlined. The mass spectrometer was used to analyse the products obtained by the methods indicated.

W. H. A.

1684. Flame propagation. 1. The effect of initial temperature on flame velocities of propane–air mixtures. G. L. Dugger. *J. Amer. chem. Soc.*, 1950, **72**, 5271–4.—It is shown that over the initial temperature range 29° to 343° C the max flame velocity of propane–air mixtures increases from 47 cm/sec to 160 cm/sec and that the rate of increase of flame velocity increases with temp. These results were found to be independent of tube dia in the range 10·2 to 22·2 mm and of stream flow Reynolds No. in the range 1500 to 2100. Approx calculations show that both Semenov's thermal theory for bimolecular reactions and the diffusion theory of Tanford and Pease predict an increase of flame velocity at an increasing rate. The relative increases predicted by the thermal theory are in satisfactory agreement with the experimental results, while those predicted by the diffusion theory are lower at the higher temperatures by as much as 35%.

W. H. A.

1685. Photographic studies of combustion. W. T. Cooper. *J. Inst. Fuel*, Mar. 1951, **24** (136), 83.—A brief review deals with four fields of combustion research, *i.e.*, fuel beds, flames, determination of temp, and furnace design, in which photography has proved most useful.

Cinematographic cameras have been used to investigate sources of heat loss in furnaces and to supply data on slag and ash formation, stoker operation, and on stratification in burning gas streams. Special techniques necessary for furnace photography were worked out in Germany. A high-speed camera was designed by R. P. Frazer for the study of flames and their propagation. Chemical reactions occurring in bunsen flames have been studied, and stroboscopic photographs of bunsen flames have been obtained. Townend, using instantaneous shadow photography, obtained a series of photographs of ignited and unignited gas streams following release from a burner. Courtney-Pratt describes an image converter tube whereby the display of the event as a function of time has been achieved, which is used in the photographic study of combustion in engines and detonation of explosives.

It has been shown that the brightness of temp of an enclosure could be determined by measuring the degree of blackening produced when the thermal radiation from the enclosure strikes a photographic plate. Two methods of photo recording of temp distribution over heated surfaces are discussed. Photographic techniques have been applied to the study of the flow pattern in a model furnace.

D. K.

1686. The heat unit. E. Griffiths. *Engineer*, 1951, **191**, 517–18.—International Unions of Physics and Chemistry have recommended that the fundamental unit of heat should be the joule (10^7 ergs), which is independent of any system of thermometry.

Conversion factors for the following four British thermal units are given: 60·5° F, mean 32° to 212° F, 39° F, steam table; and for the following five calories: international steam table, 15° C, 4° C, thermochemical or "defined," mean 0° to 100° C. Definitions and notes concerning these various British thermal units and calories are given. A table is given showing sp. ht. of water in joules per degree over the range 0° to 100° C, for use in converting thermal data which have been expressed in terms of heat capacity of water over a range of temp. A. C.

1687. Inhibition of Friedel–Crafts polymerization. I. The mechanism of inhibition. J. George, H. Wechsler, and H. Mark. *J. Amer. chem. Soc.*, 1950, **72**, 3891–6.—The polymerization of styrene was carried out with tin tetrachloride as catalyst and mono-, di-, and tri-*n*-butylamine and dimethylamine as inhibitors. Mono-*n*-butylamine was found to be the weakest inhibitor, with the other three amines being about equally effective. It is suggested that the inhibition mechanism involves the conversion of a carbonium ion to an ammonium ion, and kinetic expressions are derived for this mechanism. W. H. A.

1688. Inhibition of Friedel–Crafts polymerization. II. Factors affecting inhibitor power. J. George, H. Mark, and H. Wechsler. *J. Amer. chem. Soc.*, 1950, **72**, 3896–901.—In the Friedel–Crafts polymerization of styrene it was shown that tin tetrachloride dibutylamine complex inhibits the reaction as much as the amine itself. Examination of the effect of chloride ion on the tin-tetrachloride-catalysed polymerization of styrene showed that it had an inhibiting effect which is ascribed to reaction between the chloride ion and the growing carbonium-ion chain. Comparison of polymerization rates indicates that chloride ions are not responsible for inhibition by tin tetrachloride–amine complexes.

The efficiency of an amine inhibiter is partly determined by reaction between the inhibitor and carbonium ion on which steric affects appear to have some influence as instanced by the behaviour of mono-, di-, and tri-*n*-butylamine and dimethylaniline on the polymerization of α-methylstyrene. Polymerization rates show that the inhibiting effect increases in the order $C_6H_5NH_2 < C_6H_5N\ (CH_3)_2 < (C_4H_9)_3N < (C_4H_9)_2NH$ and that all inhibitors are weaker towards α-methylstyrene than styrene. The results are reported to be consistent with the occurrence of considerable strain in the formation of α-methylstyreneammonium ions. W. H. A.

1689. Kinetics of polymerization of styrene by Friedel–Craft catalysts. D. O. Jordan and A. R. Mathieson. *Nature*, 1951, **167**, 523.—The polymerization of styrene in CCl_4 solution when catalysed by $AlCl_3$ has been studied. It is found that: (1) the polymer formed is equivalent to the monomer consumed; (2) the polymers are of low molecular weight; (3) the overall reaction energy is small; (4) the overall rate of monomer consumption, dm/dt, is represented by $-dm/dt = k_0(m - x)\ (b - x/n)$, where x is the monomer consumed in time t, m and b are the initial monomer and catalyst concentrations, and n is the average length of polymer formed; (5) the overall constant k_0 is different for each reaction, and obeys the relation $\log_e k_0 \propto 1/n$; (6) the "catalyst" is consumed during the reaction; (7) the initial reaction rate $\propto mb$, and gives always the same reaction constant.

These results can be expressed by a chain mechanism, which is given in full, involving activated molecules. H. C. E.

1690. Some aspects of the rheology and stability of emulsions and suspensions. E. W. J. Mardles and A. de Waele. *J. coll. Sci.*, 1951, **6**, 42–56.—A review of the properties of emulsions and suspensions described in terms of molecular interaction. The following main rheological properties are discussed: (*a*) thixotropy (*e.g.*, bentonite in alcohol/water mixtures); (*b*) packing of particles and the rheology of creams and pastes (*e.g.*, aluminium powder in mineral oils); (*c*) properties of thin films (*e.g.*, aluminium powder in mineral oils); (*d*) emulsion stability (*e.g.*, the effect of lecithin in water/oil systems); (*e*) mechanical aspects.

The rheological behaviour of emulsions and suspensions is considered in relation to the properties of surface films adsorbed on the dispersed particles. Changes in the composition of mixed liquids, or small additions of high-molecular-weight substances,

produce changes in thixotropy due to changes in the character of the interfacial surface film. Increase of friction between the particles results in larger sedimentation volumes and higher surface visc.

This aspect of the theory of emulsions and suspensions, especially for the more concentrated systems, outweighs the usual approach of purely thermodynamic considerations. H. C. E.

1691. A research in rheology. E. W. J. Mardles. *Paint Manfr*, Mar. 1951, **21** (3), 90.—A brief history of the development of the British Society of Rheology is presented, together with a report of some of the more recent activities. Meetings were held wherein the main subjects under discussion were : rotary viscometers, tackiness, consistency, thixotropy, nomenclature, and symbols. There are thirteen literature references. D. K.

Analysis and Testing

1692. All-glass bubble cap column. J. C. Smith and E. F. Kelm. *Chem. Engng*, 1951, **58** (2), 155.—Tests on a single-cap 6-inch-dia column indicate that the overall plate efficiency of a commercial-glass bubble-cap column suitable for corrosive mixtures would be 39%.

Methyl *cyclo*hexane–toluene and carbon tetrachloride–benzene test mixtures were used in an unlagged column. Full structural details are given. D. H.

1692a. Determination of moisture in refrigerator oils. *Erdöl u. Kohle*, 1951, **4**, 29.—Draft German standard DIN 51552. Moisture (both free and dissolved) is swept out of the oil (maintained at 55° to 65° C) by stream of O_2-free N_2, absorbed in P_2O_5 and determined by weighing. Test duration is 12 hr for light oils ($E_{20} \not> 20°$) and 18 hr for heavier oils. V. B.

1693. Damping device for viscometers. A. O. Mathai. *J. sci. Instrum.*, 1951, **28**, 125.—A description is given of a damping device for use with suspended types of concentric-cylinder viscometers. C. N. T.

1693a. Determination of Freon-insolubles (paraffin wax) in refrigerator oils. Anon. *Erdöl u. Kohle*, 1951, **4**, 30.—Draft German standard DIN 51590. Freon (CF_2Cl_2)-insoluble material consists mainly of paraffin wax and occasionally also resinous substances. Test is carried out using 10 g oil in 100 g Freon at b.p. (−29·8° C) of latter at normal pressure. Insoluble material is filtered off, recovered by solution in hot trichlor-ethylene, and weighed. V. B.

Gas

1694. Combustible natural gas in France. V. Charrin. *Chim. et Ind.*, 1951, **65**, 565–7.—Recent (1939) gas find in Pyrénées region, yielding large quantities of gas at 160 kg/cm², is reason for stimulating search in other areas. Prospects of four zones, viz., Jura, Alps, Landes, and Limagne are discussed. In Jura small production is current, and possibilities of expansion appear good; inadequate information is as yet available concerning remaining territories, although numerous gas shows have been reported. In Limagne area any deep drilling should be carried out with circumspection, to avoid disturbance of Vichy water basin. V. B.

Engine Fuels

1695. Aviation fuels. L. Bass. *Ingenieur*, 9.3.51, **63** (10), L.13.—Deals with aviation fuels for piston engines and gas turbines, and refers to the properties of these fuels in so far as they effect engine performance. The problems arising from the use of T.E.L. are mentioned in some detail, and the influence of fuel volatility is also discussed.

In the discussion of aviation kerosines, the question of the availability of different fuel types and their influence on the economics of operation is developed at some length. Possible future sources of fuel are referred to. R. R.

Lubricants

1696. Additives and other factors that influence grease characteristics. Anon. *Oil Gas J.*, 26.4.51, **49** (51), 199.—No. 68 in the Refiner's Notebook series reviews chemical additives and percentage of soap employed, influencing grease properties such as consistency, heat resistance, oxidation stability, E.P. properties, and rust-preventive qualities. G. A. C.

1697. High temperature lubricants. Anon. *Chem. Engng*, 1951, **58** (2), 184.—Fluid silicones are in use up to 500° F; several greases are in successful use at high (300° F) and low (−100° F) temp.

Fluorothene polymers ranging from oils to waxes are finding application in handling reactive materials like liquid oxygen. Heat stability is superior to that of silicones. Prices are higher.

Molybdenum lubricants are being developed. Glycol-base compounds vaporize at 800° F, leaving 0·01% carbon. The molybdenum left behind lubricates hot extrusion dies up to 1200° F for short periods. D. H.

1698. Properties and performance of silicone lubricants. G. Grant and C. C. Currie. *Mech. Engng*, Apr. 1951, **73** (4), 311.—These days there is an increasing demand for lubricants with high load-carrying capacity and for lubricants which will withstand very high operating temp, as well as the very low temp specified for many military applications. These requirements give new significance to the properties which are characteristic of silicone fluids and of the greases compounded from them. The paper describes various silicone lubricants and fluids, and tabulates their properties. Functional tests are described which have been used for the purpose of evaluating the performance of silicone lubricants, and typical performances of the latter in practice are indicated. It is concluded from practical experience that silicone lubricants exhibit exceptional resistance to heat and to a large number of corrosive materials. They show relatively little change in physical characteristics over a wide temp span, and their load-carrying capacity may be limited or excellent, depending upon the bearing-metal combinations. Silicone lubricants have a long service life in anti-friction bearings operating at relatively high speeds under normally encountered loads at temp from −100° to +375° F, and if the bearings are relubricated the operating temp may be increased to as much as 700° F. The lubricants in question are most useful where organic oils and greases stiffen at low temp, where they break down in corrosive atmospheres, and where they bleed, evaporate, or form gums at high temp. A. S.

Bitumen, Asphalt, and Tar

1699. Bitumen decomposition with the aid of selective solvents. Part 1. K. Krenkler *et al.* *Bitumen, Teere, Asphalte, Peche*, 1951, **3** (2), 59–63.—In this, the first of a series of three articles, conventional methods of investigation of the internal structure of bitumen are examined critically and considered to be unsatisfactory. The theoretical foundation of selective solution and the sp action of various polar and non-polar solvents in overcoming the association forces and solvating the bitumen micelles are discussed. By the method described the bitumen is dissolved in xylene, which solvates the micelles completely. A suitable precipitant is added to the solution drop by drop whilst shaking, until the higher molecular constituents are pptd. Aromatics give complete solution, but solvents of medium solvation energy, saturated hydrocarbons of the chain paraffins, *iso*paraffins, and naphthenes leave a residue. *n'*-Hexane and *n'*-heptane give between 20 and 40% pptn, but only the relatively high mol constituents are separated, whilst the medium and low mol constituents remain in solution. A second cut is obtained by using the polar hydrocarbon *n'*-butanol, which dissolves only the easily solvated low mol hydrocarbons with oily characteristics and not the higher molecular and more strongly associated resinous bitumen hydrocarbons. Thus *n'*-butanol and *n'*-heptane resolve bitumen into three graded fractions. *n'*-Butanol preferably dissolves the low mol oily hydrocarbons, *n'*-heptane also the medium resinous bodies and gives a residue of high mol asphaltenic constituents. *Cyclo*-Hexane gives an indication of the presence of thermally stressed and cracked substances. R. T.

1700. Distribution of the binder in tar-fine mineral masses suitable for pouring cold. R. Siedentop. *Bitumen, Teere, Asphalte, Peche*, 1951, **2** (2), 28–32.—Production on an industrial scale to determine the improvement in binder distribution resulting from milling lean tar–fine furnace slag masses suitable for cold pouring is described. An analytical examination of the milled mass permits the following observations. In mixing, fractions of binder and filler form a cement which coats the remaining filler grains unevenly. Consolidation produces a denser mineral bedding. Thereby cement is squeezed out from the cement-rich agglomerates of medium grain size into the adjacent cavities of varying dimensions—depending upon grain shape and bedding conditions—until the mineral framework is stable. When using a definite quantity of binder, complete filling of the innumerable smaller cavities—not the larger ones—with cement may occur, giving a max mineral density. The large quantity of cement formed by using more binder cannot be taken up by the smaller cavities and fissures and, owing to its high visc, it cannot reach the distant larger cavities through the minute fissures. The densest bedding is not obtained, and a thick film of cement remains between the contact surfaces of the grains. The strength is lower than that obtained when using less binder. The " squeezing out " phenomenon in construction and traffic is anticipated by milling of the masses formerly produced in the conventional way. R. T.

1701. Natural asphalt mastic in hydraulic construction. O. Martin. *Bitumen, Teere, Asphalte, Peche*, 1951, **1** (2), 10–13.—Procedures adopted for repairing and sealing severely damaged hydraulic structures in Germany by pouring in asphalt mastic at 160° to 180° C are described. The work includes the sea-walls of Pellworm island in the North Sea, the Dortmund–Ems canal, dykes, and mine-pump cellars. The asphaltic compositions contained 16%-insulating mastic 72% (11·5% bitumen cont, set. pt. 42° C), petroleum bitumen 8% (set. pt. 28° C), dune sand 20% (total bitumen cont 19·5% set. pt. 36° C), and natural asphalt mastic 70%, petroleum bitumen 5%, dune sand 25%. Details of quantities of gravel, chips, and erratic granite blocks are given for specific repairs. Photographs and sectional drawings illustrate the operations. R. T.

1702. The importance of the process of increase in viscosity in tar and bitumen street surfacings. R. Crantz. *Bitumen, Teere, Asphalte, Peche*, 1951, **1** (2), 5–9.—Tar and asphalt road constructions fall into two categories: constructions which attain their max working val immediately on completion, and those which depend on an increase in visc of binder and orientation of the mineral framework under traffic. The first construction depends upon the characteristic properties of the hard and tough bitumens used. The second construction depends upon the evaporation of the middle oil and chemical changes caused by light and air in the case of tars, and on evaporation of the solvent in the case of cut-back bitumens. The time of visc increase and the initial visc of the tar are important when surfacing with tar. Tars which thicken quicker give better adhesion. When using bitumen the tech requirements are high wettability during construction, rapid evaporation of part of the cut-back medium, and slow evaporation of the residual solvent. Compression surfacings considered are macadam constructions and those of low porosity. The economical aspect is considered generally in choosing the stone, but the nature and granulation have an important bearing on the success of the surfacing operation. R. T.

1703. Patents. N.V. de Bataafsche Petroleum Maatschappij. F.P. 902,529, 9.3.44. Issued 3.9.45. Dutch Prior. 22.5.43. Iron varnish with diminished permeability to water and combustibility.

N.V. de Bataafsche Petroleum Maatschappij. F.P. 923,392, 5.3.46. Issued 4.7.47. Prevention of the gelatinization of bitumen solution.

C.D. Patents Ltd. F.P. 953,576, 29.9.47. Issued 8.12.49, E. Prior. 19.6.46. Moulded articles from pitch and tar.

Aktiebolaget Svenska Aluminium Co. Swed. P. 125,595. Impervious bitumen masses. R. T.

Special Hydrocarbon Products

1704. Refined petroleum oils as insecticides. E. R. de Ong. *Petroleum*, Mar. 1951, **14** (3), 64–6.—The adoption of the sulphuric acid refining process and the use of the unsulphonated residue value as a criterion has enabled the utilization of low-price and widely distributed petroleum distillates in crop protection, not only as direct insecticides but also as carriers for other toxic insecticides and fungicides. Plant tolerance is related to unsaturated compounds, and in general oils of a paraffinic character show a greater efficiency as insecticides. The article describes (1) historical development; (2) composition and plant tolerance; (3) specification of distillates, including the importance of visc, distillation range, and the possible production of organic acids by oxidation; (4) emulsions and emulsifiers used in spray practice; (5) effect of sprays on plants. R. E. P.

1705. Petroleum sulphonates. R. Leslie. *Petroleum*, Feb. 1951, **14** (2), 36–9.—The manufacture, general properties, and concentration of various types of petroleum sulphonates are described. A brief account of their many applications is included. The chief advantages of the oil-soluble petroleum sulphonates over other agents are their unique emulsifying, solubilizing, and blending properties and their low cost. The water-soluble sulphonates are mainly used where a cheap cold-water wetting agent is required. R. E. P.

1706. High toluene yield produced in Old Dutch Platformer test run. Anon. *World Petrol.*, 1951, **22** (2), 33–5.—Experimental runs on a commercial plant have shown that platforming of close-cut naphthas, *e.g.*, 202° to 224° F, containing 59·3% naphthenes, 31·9% paraffins, 8·8% aromatics can yield more than 50% of a heavy platformate containing 94% vol aromatics. Toluene yield was 41·5%. More heating capacity is required when hydrocracking is avoided, and by modifying furnaces in eleven plants, existing or projected, it is estimated that benzene shortage could be eliminated and alkylate shortage relieved by incorporating platformate in aviation blends. E. B.

1707. What replacements for carnauba wax? A. A. Kroner. *Soap Sanitary Chem.*, Mar. 1951, **27** (3), 110.—Increased prices of many waxes, particularly carnauba wax, are forcing manufacturers to find cheaper substitutes for use in their products. Five kinds of wax are available as replacements for carnauba: animal waxes, vegetable waxes, synthetic waxes, petroleum waxes, and composition waxes. The specifications for these waxes do not give a complete picture of their characteristics. For instance, nothing is said about the compatibility of a given wax with the other components of the formulation in which it is to be used. To facilitate comparison between various waxes this article includes tables giving average chemical and physical data for representatives of each class of wax, and then continues to describe substitutes which have been found suitable in emulsion and paste formulations. O. M.

Coal, Shale, and Peat

1708. Development of low-temperature carbonization of coal. G. S. Pound. *J. Inst. Fuel*, Mar. 1951, **23** (136), 61.—A condensed review of the progress of low-temp carbonization of bituminous coal during the first half of this century. Research is directed to the means of improving efficiency of the carbonizing process and to the production of pure chemicals; various pilot plants have been erected. Types of low-temp carbonization processes are classified according to types of retorts used, *e.g.*, vertical retorts, rotary retorts, producer-type retorts, conveyor retorts, and miscellaneous—each type is briefly discussed. The temperature of carbonization affects not only the physical properties of resultant coke but also the yield and composition of gaseous and liquid by-products. Most workers in the low-temp-carbonization field have adopted a carbonization temp in the range 550° to 600° C. The properties of an ideal low-temp fuel are listed. The history of one successful low-temp carbonizing process (Parker) and a description of the present plant are given. The working up of crude liquid is discussed, particularly at Bolsover refinery, distillation of crude oil, continuous tar-acid recovery plant, diesel-oil refinery plant, pre-treatment, carbonating

and springing plants, causticizing, and a cresylic acid distillation plant are particularly considered.

Recent plant developments include trixylenyl phosphate plant, tar acid chlorination plant, continuous tar acids fractionation plant, liquor-treatment plant, and extract-treatment plant.

Also discussed are process additions and modifications and research and development. D. K.

Miscellaneous Products

1709. Scabrin—a new botanical insecticide. R. C. Roark. *Soap Sanitary Chem.*, Mar. 1951, **27** (3), 125.—From the roots of the plant *H. scabra* there has been isolated a viscous yellow oil which has been designated scabrin. It occurs in the dry plant to the extent of some 0·2% wt., and is believed to be closely related to *n-iso*butyl-2 : 6 : 8-decatrienamide, which has been found to be present in the roots of *H. longipes*. Scabrin is 2·5 times as toxic as pyrethrins to houseflies, but appears to be also toxic to warm-blooded animals. Tests on it and allied substances are continuing. O. M.

1710. Styreneless rubber. Anon. *Chem. Engng*, 1950, **57** (9), 107.—Polybutadiene rubber is superior to GR-S on road test when made by a modified low-temp process. Details of the process are given with operating times and temps. D. H.

1711. Vinyl resins. C. F. Ruebensaal. *Chem. Engng*, 1950, **57** (12), 102–5.—The manufacture from acetylene and HCl gas of vinyl chloride, and properties of the polymer, are described. Such problems of operation as purification by ion exchange and removal, polymerizing agent corrosion, handling of polymer suspensions, centrifuging, removal of tramp iron are overcome. Uses of the polymer are mentioned. D. H.

1712. Quaternaries in hard water. E. W. Dennis. *Soap Sanitary Chem.*, Mar. 1951, **27** (3), 117.—Since no test has been available for the bactericidal evaluation of quaternary ammonium germicides, an investigation has been carried out with a view to establishing a suitable procedure. In this investigation, which included *in vivo* and *in vitro* procedures, benzalkonium chloride has been used as the model of its class of disinfectants. The following conclusions have been reached.

1. The highly virulent g positive haemolytic streptococcus pyogenes C-203 M and the g negative *Pasteurella boviseptica* are suitable representative test organisms for *in vivo* challenge of germicidal activity. *Salmonella typhosa* Hopkins can be used as a test organism, but the problems created by its low pathogenicity for mice make it unsuitable for routine use.

2. Benzalkonium chloride at a concentration of 200 p.p.m. is an efficient anti-infective agent against the above pathogenic bacteria.

3. The anti-infective properties of the quaternary are not reduced below a required concentration of 200 p.p.m. even when used in very hard waters. The period of exposure was approximately 2 min, and a blood-broth inoculum of streptococci or *Pasteurella* provided 0·5 to 1·0% whole blood as extraneous organic matter. O. M.

1713. Some aspects of the oxidation of the drying oils. L. Williamson. *J. Oil Col. Chem. Assoc.*, Mar. 1951, **34** (369), 119.—Oxidative polymerization is a major factor in the gelation of oils and oil-modified resins through the formation and decay of the peroxide group. A study has been made of the oxidation of simple methyl esters of unsaturated fatty acids. The mechanism appears to be one of dimerization through the immediate formation of free radicals. Reaction of the esters in a neutral liquid phase with gaseous oxygen and reaction in a homogeneous liquid phase consisting of an active oxygen-containing compound together with a polar medium are discussed. In the early stages of oxidation the products of thermal decomposition are dimers with double bonds, hydroxy and some ketonic compounds. Later many other oxy-compounds are formed, particularly if conditions are favourable to a polar reaction. Catalysts may be considered as primary or secondary. Primary catalysts accelerate

the primary oxygen uptake, whilst the secondary catalyst accelerates the peroxide decomposition. It is thought that the triglyceride oil molecule should react in a similar way to the methyl esters. D. K.

1714. Alkali attack on paint. G. W. Mack. *Paint Mnfr*, Apr. 1951, **31** (4), 121.—Alkali attack on oil paints upon building materials generally occurs only in the presence of lime, moisture, and certain salts. Chlorides, sulphates, and carbonates of sodium and potassium stimulate attack in the presence of lime. Porosity of the background may have considerable effect on attack; backgrounds of low porosity are less liable to be affected. Alkali attack can occur when other alkalis replace lime and activating salts, *e.g.*, sodium silicate.

The mechanism of the activation of lime by various salts can be explained by use of the solubility product and extended Debye–Huckel equation. As these concepts are often limited in accuracy in concentrated solutions, a practical study of solutions containing excess of a commercial hydrated lime with added salts was made. The following hypothesis was put forward to explain the known characteristics of alkali attack: the rate of alkali attack is governed by the activity of metal hydroxide in the solution in the pores of the background and by the ease of diffusion in that solution. Four possible pretreatments suggested are: (1) neutralization of alkali, (2) addition of repressive salts, (3) plugging the surface, (4) treatment with reagents which precipitate the alkali metal. These methods give some measure of protection but do not safeguard against drastic conditions. Other possible remedies discussed are use of materials free from alkali, salt, or lime, control of moisture and insulation by alkali-resistant primers.

Immunity from attack necessitates a permanently thoroughly dry background; a partial use of this principle lies in the use of porous paints. Impermeable alkali-resistant primers can be successful, but may fail in other ways if conditions are damp. D. K.

Corrosion

1715. Corrosion and its control. M. E. Parker. *Oil Gas J.*, 19.4.51, **49** (50), 244.—Part 8 of this series concerns cathodic protection of condensers and heat exchangers. Bimetallic corrosion set up by presence of alloy tubes and steel tubes, sheets, headers, and shells can be successfully combated by installation of magnesium anodes in the water-box.

Rods of extruded magnesium alloy may be installed in pipe plugs screwed into openings in shell.

Exposed area of metal should be provided with 10 mA/sq. ft. G. A. C.

1716. Corrosion prevention in the manufacturing process. J. R. Fawcett. *Mech. World*, 27.4.51, **129** (3354), 381.—The loss of iron and steel through corrosion is estimated at 40% of a year's pig-iron production. The monetary value of this loss is far greater than the value of the iron and steel, since serious corrosion of a main structure may cause it to be abandoned together with many auxiliary parts which would, otherwise, be still serviceable. There is also a continuous expenditure on carrying out repairs and making replacements of corroded parts. To-day there is no excuse for producing goods which fail by corrosion before the end of their potentially useful life. Serious consideration should be given at the design stage of the problem of corrosion prevention. All effective methods of protecting mild steel from corrosion depend on the removal of all grease and rust from the surface and the application of a protective coating. One of the most common and effective processes for preparing steel prior to finishing is sand or shot blasting. Pickling in acid is also widely used, the parts being immersed in hot sulphuric or cold hydrochloric acid. Pickling in acid leaves a finer surface than does shot blasting, and there is no danger of mechanical damage. However, care must be taken to remove all the acid from the surface. After either of these processes, a protective coating must be applied almost immediately, otherwise further corrosion will occur. Existing structures cannot be dealt with by either of the above methods and a special oxy-acetylene torch with a batswing flame must be used. Phosphate coatings might also be used for preparing corroded surfaces. Methods of applying corrosion-resistant surfaces include electroplating, hot dipping

in tin or zinc, metal spraying, dull chemical finishes, painting, and vitreous enamelling. By far the most important finishes in terms of surface area are the paints, varnishes, and lacquers. The advantages and disadvantages of the various methods listed are described. A. S.

1717. Corrosion resistance of copper and copper alloys. Anon. *Chem. Engng*, 1951, **58** (1), 108–12.—Summarizes resistance of copper alloys to acids, alkalis, ammonia, salt solutions, gases, organic compounds, water, petroleum, and steam. Coded alloys are bracketed when equivalent, and suitability for a particular duty may be found from a chart. The recommendations are not final, however, since local conditions and trace elements are not included. D. H.

1718. Organic corrosion preventive. C. M. Blair. *World Oil*, Nov. 1950, **131** (6), 159.—Although methods of application vary widely, corrosion, once considered inherent in the production of oil, is now controlled to an even larger extent by the use of organic preventives. These are available in both liquid and stick forms, and form the basis of the two principal methods of application described in the paper. For wells with open casing, liquid application is more widely practised, while the stick form is more suitable to wells having a casing closed by a packer.

The preventive may be introduced into the well continuously or intermittently, depending on local conditions. For high-pressure gas and gas-condensate wells, a lubricator must be used. The use of stick preventives is convenient for such wells. The rate of corrosion must be estimated to enable the requisite application to be determined: common practice is to commence the operation by an initially high dosing. In the majority of cases of highly corrosive produced oil a concentration of 1 part preventive to 5000 parts of produced oil gives adequate protection; corrosion has been reduced by as much as 98% by such application. Parallel improvement was obtained in the case of a condensate well, data of which are given graphically.

Arrangement of equipment is explained with the aid of diagrams. References. A. J. H.

1719. Clad steel equipment—some hints for modern maintenance. E. H. Wyche. *Chem. Engng*, 1951, **58** (1), 122–3.—The cleanliness of the surface of stainless-steel and high-nickel-clad equipment is of extreme importance in reducing corrosion. Rough surfaces tend to hold up corrosive moist solutions which set up concentration cells. A list of less obvious causes of corrosion contains items such as the effect of graphite pencils in marking out and tools dropped on to the surface during construction.

Mild and drastic cleaning agents for stainless-steel, nickel, and monel tanks are formulated. Special pastes are described for polished surfaces. D. H.

1720. Determination of current requirements for cathodic protection. M. E. Parker. *World Oil*, Nov. 1950, **131** (6), 253.—Estimates of cost of cathodic protection must necessarily be preceded by the calculation of current requirements, by actual field test, or in some cases by a combination of the two methods. Protection of bare metal surface of pipelines could be effected by a current equivalent to about 2 mA/sq. ft. exposed, but such complete protection is never contemplated. A well-coated line may be said to be 2% bare.

Emphasis is laid on practical details. The use of magnesium anodes is favoured, as it gives more representative data; it also requires longer time. The field of cathodic protection may extend also to partly coated pipelines, and to tank bottoms. The principal difficulty with the latter lies in obtaining sufficient information relating to the inaccessible metal surfaces; polarization is slow.

Sea-water structures, although surrounded by a medium of relatively constant resistivity, are subject to surface wear and organic growths. Calculations of required current are based on 50% bare metal, and should allow for possible extension to give 100% protection.

Other minor applications are mentioned. References. A. J. H.

1721. Dow draws conclusions from three-year paint study. O. K. Sieplein. *Chem. Engng*, 1950, **57** (10), 110–15.—Summarized are the chief pigments and their colour-retention properties. Many combinations of primer and finish were tested under different climatic and corrosive conditions, and the results of tests indicate which combinations are most suited for a particular duty. D. H.

Engines and Automotive Equipment

1722. Two Sulzer diesel railway [engines]. Anon. *Gas Oil Pwr*, 1951, **46**, 100.—Three 960-h.p. diesel-electric locomotives have been constructed for the Siamese State Railways. Each is powered by a Sulzer pressure-charged 8LDA25 unit of eight cyl of bore and stroke 250 and 320 mm respectively. The unit develops 960 b.h.p. at 850 r.p.m. as a 1-hr output, and 860 b.h.p. at 800 r.p.m. as a continuous output. The unit drives a 550-kW main generator operating at 800 r.p.m. and a 33·7-kW auxiliary generator which supplies the main generator excitation current and ancillary engine equipment.

Five diesel electric railcars for North Africa are powered by 6LDA25 six-cyl units similar in design and construction to the units described above. Sea-level output of a single unit is 735 b.h.p. at 850 r.p.m. on the 1-hr rating, and the railcar develops 1470 b.h.p., giving a top speed of 81 m.p.h. with a trailing load of 150 tons. H. C. E.

1723. Diesel locomotive manufacture in the United States. Anon. *Gas Oil Pwr*, 1950, **45**, 338–42.—A summary of the report issued by the productivity team of the diesel locomotive manufacturing industry which visited the U.S.A. in the early part of 1950. H. C. E.

1724. Fuel peak pressure indicator. Anon. *Gas Oil Pwr*, 1951, **46**, 87.—This instrument is used for measuring oil-engine fuel-injection pressures up to 15,000 p.s.i., and should provide warning of incipient choking in atomizers.

In operation the fuel acts on a spring-loaded plunger to force it upwards, thus lifting a conical nut from its seat. The conical nut is connected with a graduated thimble, and when free this rotates under the influence of a clock spring. The thimble is graduated in 100-lb divisions to 10,000 p.s.i., and there is a further graduation at 15,000 p.s.i. H. C. E.

1725. Opposed-piston machinery. W. H. Purdie. *Motor Ship*, Apr. 1951, **32** (373), 37.—Article is an extract from 23rd Thomas Lowe Gray lecture read at a meeting of the I. Mech. E. History and development of opposed-piston propelling machinery is traced, from the time thirty years ago when first Doxford opposed-piston marine oil-engine commenced trials on the test bed to present day. U. M.

1726. Automotive turbine progress. Anon. *World Petrol.*, 1951, **22** (2), 50, 52.—Turbine engine 200 lb in weight, 175 h.p. compressor speed 36,000 r.p.m. has been developed by Boering, and is undergoing tests in a 10-ton truck. Fuel consumption is approx 1·25 lb/b.h.p.-hr, and is expected to be reduced to 0·70 (c-f. 0·45 for a diesel engine). There are only 220 parts in the engine, and the installation envelope is 9·4 ft³. E. B.

1727. Progress review No. 15 : Gas turbines. D. N. Mallinson. *J. Inst. Fuel*, Mar. 1951, **24** (136), 76.—Developments in the use of gas turbines for aircraft, locomotives, road traction, ships, and current generation since Nov. 1948 are reviewed.

Aircraft powered by pure jet propulsion and others with propeller turbine engines have come to the fore. Aircraft turbines manufactured by various British companies are described. There is a trend towards the use of axial compressors even for aircraft application. The use of combustion systems with a number of separate combustion chambers continues to be the general practice. Fuel is almost invariably standard aviation kerosine. Recently information has been published on exhaust reheat, the work having been carried out by the National Gas Turbine Establishment. In Britain one gas-turbine locomotive is being built by Metropolitan Vickers for B.R. Western Region. American locomotive projects are discussed. A table is presented of gas-turbine locomotives for Great Britain, Switzerland, and the U.S.A.

Mention is made of the Rover gas-turbine car and the use in America of the Boeing 200-h.p. engine as power-plant for a heavy goods vehicle. The problem of gas turbines for road traction is discussed.

Marine gas turbines under construction and test in Great Britain, France, Switzerland, and U.S.A. are listed and described.

Tables showing country, user, power, etc., of gas turbines for current generation and experimental units are presented. The Swiss power-stations Beznau and Weinfelden are considered in some detail. Gas turbines for the Scottish hydro-electric Board are being designed. Little work is being done in America on the use of this type of power unit for power-stations, and on the Continent, except for Switzerland, work is still in the experimental stage. D. K.

1728. Gas turbine operating experience. G. B. R. Feilden. *Motor Ship*, Apr. 1951, **32** (373), 20.—Results and conclusions derived from twelve months' running of 750-kW open-cycle gas turbine, built by Ruston and Hornsby, are presented. Novel design features of unit enumerated, and overall performance figures summarized graphically. Details are given of examination findings, and modifications carried out, on effects on compressor blading, the combustion system, deposits on turbine, and distortion problems. U. M.

1729. The relative merits of centrifugal and axial compressors for aircraft gas turbines. E. S. Moult and H. Pearson. *J. Royal Aero. Soc.*, 1951, **55** (483), 129.—An account of a discussion at which four short papers were presented. Supporting speakers were J. L. Brodie and A. C. Lovesay, and the contributions made by others are also included. In the first paper the centrifugal compressor is considered from the aspects of performance, time of development, production cost, and serviceability. In the second, factors such as efficiency, air mass flow per unit frontal area, weight and compactness for given duty, flexibility, reliability, and cost are considered, quantitative data illustrating various points. Production aspects are discussed in more detail in the third paper, which gives additional information about vulnerability to ice, etc., overhaul periods, compressor fouling, fuel consumption, and erosion. In the fourth paper data based on 8000 hr running (2500 hr flight) are given in a review of performance of axial compressors. C. N. T.

1730. New high-pressure turbo-charged M.A.N. engine. Anon. *Gas Oil Pwr*, 1951, **46**, 85, 86, 91.—This experimental crosshead four-stroke engine has six cyl of bore and stroke 300 and 450 mm respectively. Designed for running at 300 to 400 r.p.m., it is now operating at 428 r.p.m.

The exhaust gas turbo-charger is specially designed. The exhaust gas turbine, of output 350 b.h.p. at 15,000 r.p.m., has five stages and the blower ten, of which nine are axial and one radial. The air is cooled between the axial and radial stages by an intercooler, and again before it enters the inlet manifold. This arrangement gives an increase of output from 750 to 1400 b.h.p., the latter corresponding to a b.m.e.p. of 213 p.s.i. The charging air pressure is 16·9 p.s.i., and the exhaust temp is 950° F. The fuel consumption is 0·312 lb/b.h.p/hr at an output of 1360 b.h.p., and the lub oil consumption is 0·0175 lb.

The engine has also been run for a short period at a b.m.e.p. of 340 p.s.i.

A short description of the engine construction is included. H. C. E.

Safety Precautions

1731. Fusion-welded pressure vessels. Anon. *Fluid Handling*, Oct. 1950 (11), 335.—This condensation of the discussion by Inst. Chem. Engrs on British Standards Code 1500 : 1949 follows its history and outlines its scope. Three classes of certainty were set up according to the hazards involved and the risk to life and limb in the event of failure. The effect of corrosion in the chemical industry warranted an extra margin of safety above that provided by API–ASME code. A draft provisional code was therefore proposed for the approval or amendment of industry, based on API–ASME code.

The latest draft code was intended to be comprehensive and versatile, providing more economical vessels not by reducing the margin of safety, but by more detailed specifications which demand better workmanship. The materials to be used are more closely defined, especially for toughened and stainless steels.

Some criticisms are made about sections of the code in particular over the properties of stainless and carbon steels, the shapes of the ends of pressure vessels, and the specification for sub-zero temperature work. D. H.

1732. New liquid skin cleansers for workers exposed to mineral oil. L. N. Savidge and F. H. Tyrer. *Brit. J. Industr. Med.*, 1951, **8**, 26–8.—Abrasive and solvent cleansers, whilst effective, are undesirable owing to damage to and defatting of skin. Work of Cruickshank (*ibid.*, 1948, **5**, 204) is discussed, and modification of cleanser proposed by him is put forward, this is 50% wood flour, 48% powdered soap, 2% borax. Liquid cleansers have, however, several advantages (*e.g.*, ease of dispensing), and suggested recipe is detergent (non-ionic, polyethylene oxide type) 24%, white mineral oil 10%, lauryl alc 5%, *iso*propyl alc 10%, cresol 2%, soap (low titre) 8%, H_2O 41%. Cheaper modification (almost as effective) is detergent (as before) 14½%, soap 5%, *iso*propyl alc 4%, H_2O 76½%. Cleansing efficacy can be verified by fluorescence of residual oil when skin is examined by U.V. light. V. B.

Miscellaneous

1733. Agreement for the sale of "know-how." T. A. Blanco White. *Conveyancer and Property Lawyer*, 1951, **15**, 89–95; 509–17.—Distinction between agreement for supplying technical information and assistance and a patent licence is considered. Unless patent validity is free from doubt it may be preferable to exclude patent licences from a "know-how" agreement, this can have advantages for the seller from a taxation aspect and also in avoiding possible difficulties arising from ss.57,58 of the Patents Act, 1949. A suggested form for agreements of the type discussed is given. V. B.

1734. Financial significance of fractional analysis. H. H. Beeson. *Oil Gas J.*, 19.4.51, **49** (50), 172.—The dependence of accurate fractional analysis of inlet gas-stream composition upon sound plant design and efficient operation and significance of such analysis as translated into plant investment and operating cost is discussed.

For example, the inlet-gas analysis is of great importance in designing type of plant recovery system; and is the determining factor as to whether the plant should produce only L.P.G. from light ends, produce mixed butane and propane, or produce normal butane, *iso*butane, and propane. G. A. C.

1735. Oil industries exhibition. C. A. Fothergill. *Nature*, 1951, **167**, 594.—A short description of the exhibition held in London, Glasgow, Leeds, and Cambridge during 1951. The exhibition is divided into the sections: oilfield exploration and development, transport, refining and manufacture, and distribution and products. H. C. E.

1736. Petroleum and European recovery. V. Smith. *Fluid Handling*, Oct. 1950, (11), 331–4.—(See Abs. No. 1357.) D. H.

1737. Review of the West German mineral oil industry in 1950. F. Below. *Bitumen, Teere, Asphalte, Peche*, 1951, **1** (2), 3–4.—During 1950 output in the various branches of petroleum production, mineral oil processing, power-fuel production, and by-product manufacture has in many cases reached max capacity. On the basis of the 1936 figures, production shows an average increase of 55%. Benzene and its homologues alone show a production below that of 1936. Relevant data are tabulated. Limitation of the production of synthetics and current mineral oil taxation are criticized. The effect of the international political and economic situation and future prospects are discussed. R. T.

1738. Sizing process equipment. P. S. Buckley. *Chem. Engng*, 1950, **57** (9), 112.—The statistical method is described of relating the uncertainties of individual data to the probability of any given design being inadequate. It enables calculation of the amount of over design necessary to reduce the risk of failure to the desired figure. A heat exchanger and a bubble-cap fractionator are used as numerical examples. D. H.

1739. Sweden's well-organized refining industry. R. L. Simons. *World Petrol.*, 1951, **22** (2), 46–9.—Sweden's refinery capacity is 1·1 million tons/year, a third of country's requirements; divided between two refining companies. One company

at Nynasham (550,000 tons) and Malmo (60,000 tons) produces all normal products, lub oils, and electrical oils. At Gothenburg the second company produces gasoline, naphtha, kerosine, diesel, and residual fuel. Naphtha is reformed and blended with S.R. gasoline to give the standard grade 79 O.N. (Research). E. B.

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Bituminous Roads in North America. Research and Construction. A. R. Lee. Road Research Technical Paper No. 22. London: H.M.S.O., 1951. Pp. 28. 2*s*. 7½*d*. post free (U.S.A., 65 cents).

Preliminary Report on Coal Suitable for the Manufacture of Synthetic Petroleum. A. B. Dutt, P. K. Ghosh, G. N. Dutt, and K. D. Shukla. Calcutta: Government Press, 1950. Pp. 109.

American Society for Testing Materials, Proceedings, Vol. 50, 1950. Committee Reports; Technical Papers. Philadelphia, Pa.: ASTM, 1951. Pp. 1490.

American Society for Testing Materials, 1950 Supplement to Book of ASTM Standards, Part 3. Cement, Concrete, Ceramics, Thermal Insulation, Road Materials, Waterproofing, Soils. Philadelphia, Pa.: ASTM, 1951. Pp. 350.

APPLICATIONS FOR MEMBERSHIP OR TRANSFER

JULY 1951

The following have applied for admission to or transfer of membership in the Institute. In accordance with the By-laws, the proposals will not be considered until the lapse of at least one month after the publication of this *Journal*, during which time any Fellow, Member, Associate Fellow, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of the candidate.

The object of this information is to assist the Council in grading the candidate according to the class of membership.

The names of candidates' proposers and seconders are given in parentheses.

Applications for Membership

COUNT ALBIZ, director, Azamon S.A. (I.C.I.). (*C. A. P. Southwell; G. Sell.*)

AMIN, Abdel Baki, engineer, Shell Co. of Egypt Ltd. (*A. D. Cooper; A. E. Badu.*)

ARTHUR, Kenneth Bismark, assistant physicist, Iraq Petroleum Co. Ltd. (*A. H. R. Grimsey; H. A. Freeman.*)

BRAKEL, Arie, chemical engineer, Shell Oil Concessions Ltd. (Venezuela). (*H. I. Waterman; J. T. N. Perquin.*)

BURNAND, Donald William, technical assistant, Messrs. W. B. Dick & Co. Ltd. (*R. F. A. Baldwin; P. M. Gossling.*)

CROSSLAND, Cyril, technical representative, British Ropes Ltd. (*P. Hutchinson; B. J. Ellis.*)

DE LESTANG, Robert Marie Clement Nageon, manager, Technical Department, Shell-Mex Brazil Ltd. (*R. G. Mitchell; G. J. Gollin.*)

DEVENISH, Harold Charles, operations manager, Trinidad Oilfeld Service Ltd. (*P. E. T. O'Connor; A. S. Curlet.*)

DUGGAN, James Daniel, chief rig erector, Anglo-Iranian Oil Co. Ltd. (*A. B. Cameron; W. G. Baillie.*)

ELLEDGE, Everard A., engineer, E. B. Badger & Sons (G.B.) Ltd. (*J. T. T. Robinson; W. R. Sharp.*)

FITZPATRICK, Henry Denis Neil, plant superintendent, Trinidad Leaseholds Ltd. (*A. S. Curlet; K. W. Barr.*)

GREEN, Donald Clare, technical officer, Caltex Oil (Aust.) Pty. Ltd. (*L. O. Shiels; H. A. Ruffell.*)

KING, Robert Charles Martin, laboratory assistant, Defence Research Laboratories, Australia. (*H. A. Ruffell; L. O. Shiels.*)

The Hon. FREDERICK ALAN LEATHERS, deputy chairman, Messrs. Wm. Cory & Son Ltd. (*Lord Leathers; Sir Hubert Heath Eves.*)

MCFADYEN, William Tennent, technical advisor, Australian Commonwealth Public Service. (*G. E. Mapstone; E. W. Sheel.*)

MCGEOCH, James D., engineer, Messrs. Costain-John Brown Ltd. (*S. E. Coomber; G. D. Hobson.*)

MATHESON, Alexander, prospector, Consolidated Diamond Mines of S.W. Africa Ltd. (*Prof. Madwick; Mr. Spencer.*)

NORTH, Thomas Roger, agent, Messrs. D. & C. and William Press Ltd. (*F. M. V. Bell; E. J. Horley.*)

OLD, Charles Henry, engineer, Anglo-Saxon Petroleum Co. Ltd. (*O. F. Thompson; R. C. H. Toye.*)

ORR, Albert Stanford, director (Refinery Technology Laboratory), Gulf Oil Corporation. (*J. O. Maskell; T. J. Metcalf.*)

RICHARDS, Richard John Cenydd, assistant constructional engineer, National Oil Refineries Ltd. (*F. V. M. Bell; E. J. Horley.*)

Ross, Ronald Keith, chief technical officer, Caltex Oil (Aust.) Pty. Ltd. (*L. O. Shiels; H. A. Ruffell.*)

Russell, Alexander Macfarlane, sales director, Messrs. Charrington, Gardner, Locket (Wholesale) Ltd. (*J. T. B. Bookey; A. G. Engelbach.*)

Seabright, Kenneth George Whitina, chemist, Attock Oil Co. Ltd. (*B. A. Raper; G. Sell.*)

Tambling, Douglas Wilfrid, Flight Lieutenant, Royal Air Force (Equipment Branch). (*C. G. Woolven; G. Sell.*)

White, Wilfred Ronald, progress and cost control engineer, "Shell" Refining & Marketing Co. Ltd. (*W. A. Laverick; J. G. Hancock.*)

Zenner, Mervyn Cameron, chemist, Defence Research Laboratories, Australia. (*H. A. Ruffell; L. O. Shiels.*)

Transfer

Edwards, Francis Dare, chemical engineer, Trinidad Leaseholds Ltd. (*A. J. Ruthven-Murray; P. H. B. Trasler.*) (*Member to Fellow.*)

NEW MEMBERS

The following elections have been made by the Council in accordance with the By-laws.

Elections are subject to confirmation in accordance with the By-laws.

As Fellow

Viktorsson, J. H.

As Member

Van Wageningen, G.

As Associate Fellows

Andrews, E.
Carlile, J. H. G.
Doggett, D. S.
Fraser, A. M.
Nair, C. N.

Transferred from Associate Member to Associate Fellow

Clarke, A. H.

Transferred from Students to Associate Fellows

Baddeley, A. R. W.
Rule, P. L.

As Associate Members

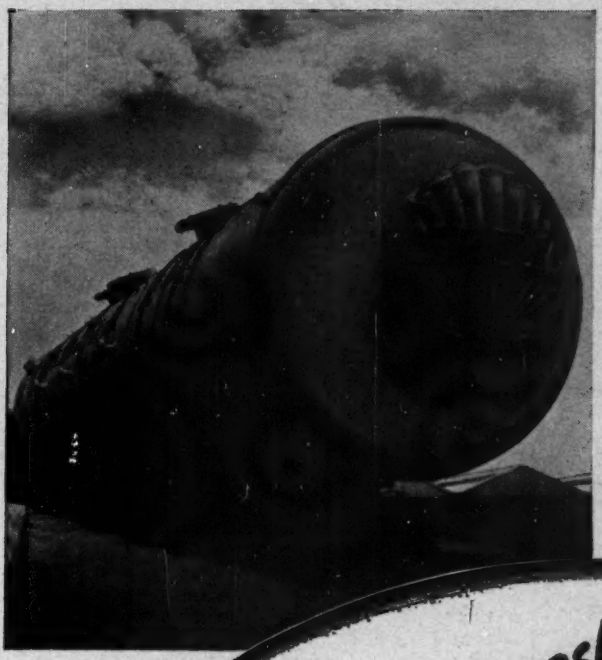
Irwin, D. L.
Moscisker, J.
Selina, A.
Sweeney, J. N.
Walsh, A. J. P.

As Students

Allen, D. V.
Edden, J. J.
Hale, A. R.
St. Leger, J. A.

As Member Company

The United Overseas Petroleum Co. Ltd.



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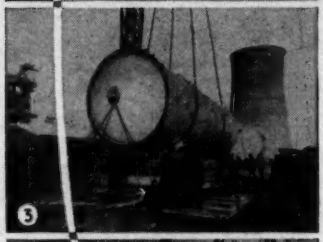

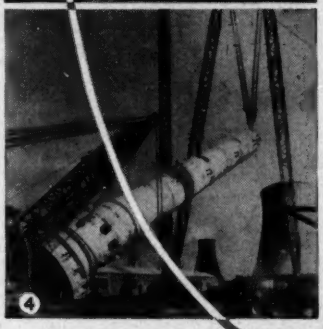

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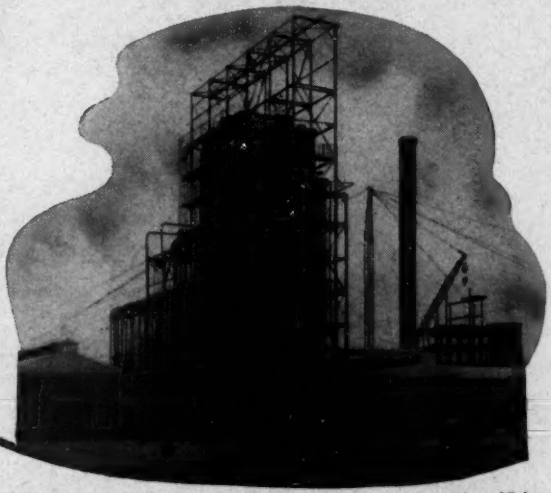

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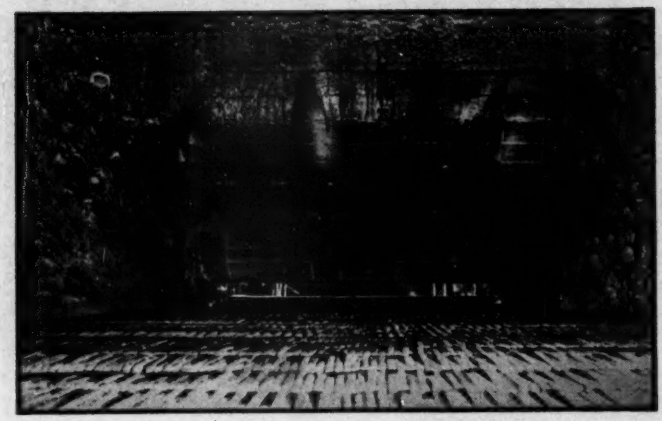

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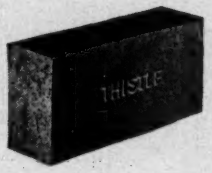

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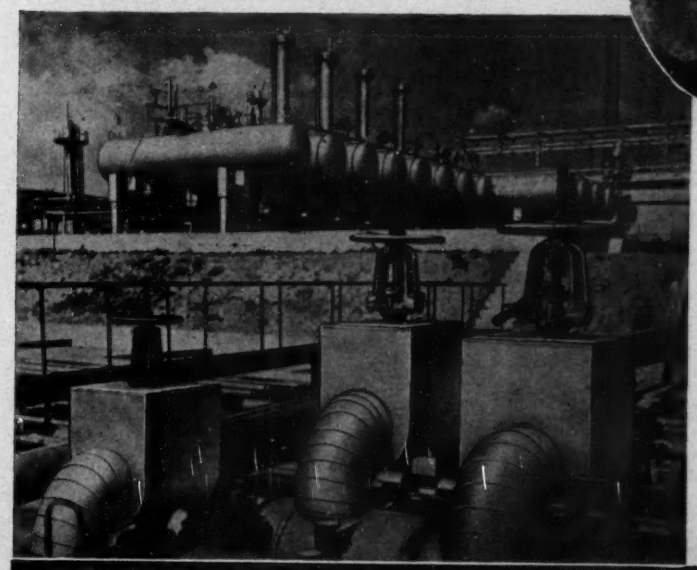

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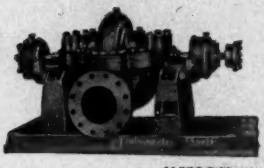

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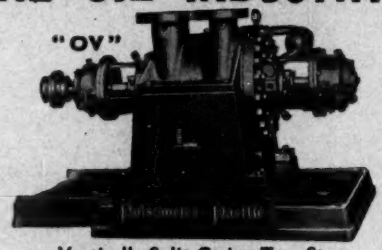

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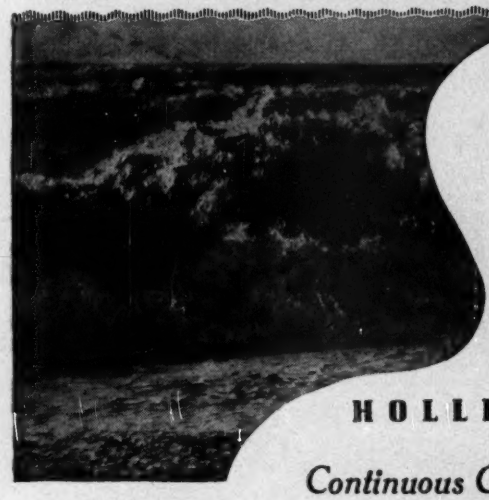

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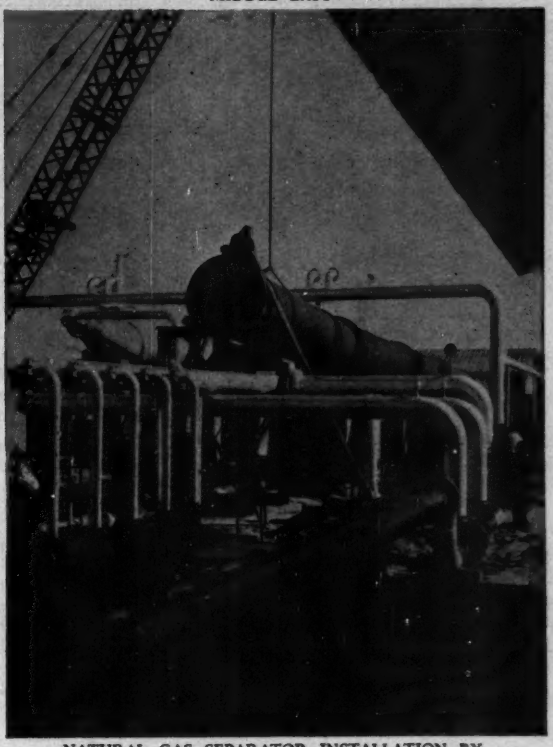

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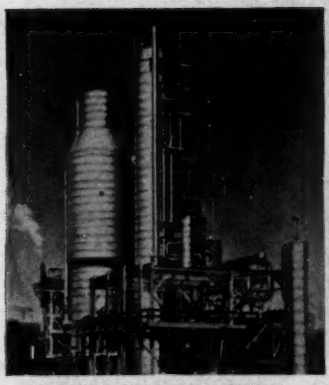
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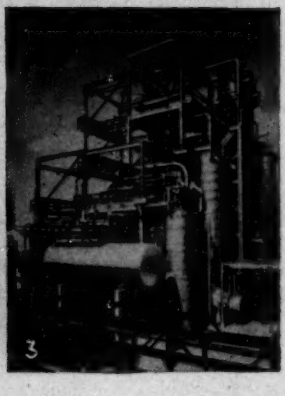
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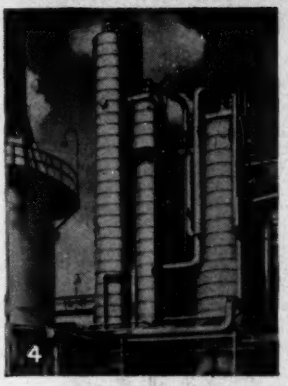
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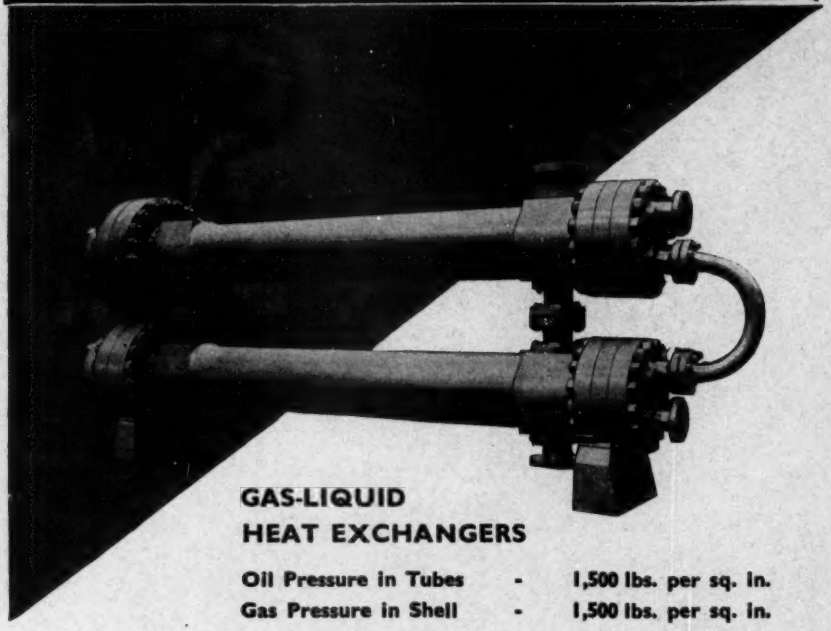

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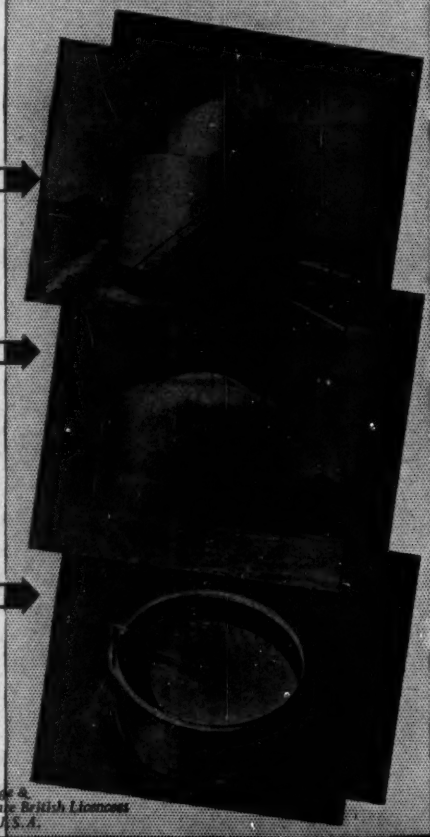

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